ANALYTICA CHIMICA ACTA

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SUBJECT INDEX

Chr. = Chromatography — chromatographie — chromatographische Analyse
Col. = Nephelometric and colorimetric analysis — Néphélométrie et colorimétrie — nephelometrische und kolorimetrische Analyse
Grav. = Gravimetric analysis — gravimétrie — gravimetrische Analyse
Id. = Identification reactions — identification (réactions) — Identifizierungsreaktionen
M. = Miscellaneous — divers — Verschiedenes
Pol. = Polarography — polarographie — Polarographie
Pot. = Potentiometric, conductometric, amperometric and coulometric analysis — potentiométrie, conductométrie, ampérométrie et coulométrie — potentiometrische, konduktometrische, amperometrische und coulometrische Analyse
Sp. = Spectrographic (spectrochemical) analysis — spectrographie — spektrographische (spektrochemische) Analyse
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A STUDY OF THREE SUGGESTED REAGENTS FOR THE DETECTION OF POTASSIUM

by

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No. T.P.

Three reagents which have been proposed for the detection of potassium have been examined, since details of sensitivity and interference are not given in the original papers. The reagents which have been studied are sodium cobalti-thiosulphate, used by CELSI[1], sodium-calcium ferrocyanide and sodium-uranyl chromate, both used by GASPAR Y ARNAL[2,3,4]. The object of the study was to determine the sensitivity of the reagent for potassium when this is the only cation in solution, the reaction, if any, between the reagents and some other cations, and the change of sensitivity of the reagents when potassium is in a solution in the presence of certain other cations.

The table shows sensitivities for potassium, reactions with other ions and the influence on the sensitivity of the reagent for potassium in presence of some other ions, compared with sodium cobalti-nitrite, an established reagent for potassium.

Reagent	Sensitivity for K	Precipitates with	No precipitate with	Change in sensitivity
Sodium cobalti-thiosulphate	1 : $1.33 \cdot 10^2$ (in pure methanol) 1 : $1.81 \cdot 10^2$ (in tech. methanol)	Rb^+ Ba^{+2} (BaS_2O_3)	Li^+, Cs^+, NH_4^+ Ca^{+2}, Sr^{+2}, Mg^{+2}	No change in presence of 10× Li^+ or NH_4^+
Sodium-calcium ferrocyanide	1 : $1.25 \cdot 10^3$	Rb^+, Cs^+, NH_4^+	Li^+ Sr^{+2}, Ba^{+2}, Mg^{+2}	No change in 10 × Li^+
Sodium-uranyl chromate	1 : $1.25 \cdot 10^3$	Rb^+, Cs^+, Ba^{+2} ($BaCrO_4$)	Li^+, NH_4^+ Ca^{+2}, Sr^{+2}, Mg^{+2}	No change in presence of 10× Li^+ or NH_4^+
Sodium cobalti-nitrite[5]	1 : $1.5 \cdot 10^5$ (microscopic technique)	Rb^+, Cs^+, NH_4^+	Li^+	Li^+ reduces sensitivity by one tenth in equal concn. to K^+

EXPERIMENTAL

1. The sodium cobalti-thiosulphate reagent has to be made up immediately before use. The method given by CELSI[1] was followed exactly, *viz.* one drop of a solution of 19 g of sodium thiosulphate in 50 ml of water and one drop of a solution of 7 g of cobalt nitrate in 50 ml of 80% methyl alcohol were added to 10 ml of methyl alcohol. A pale violet solution was formed on mixing. One to four drops of the solution containing potassium was added to the reagent so prepared. In the presence of potassium at a suitable concentration, a sky-blue precipitate of potassium cobalti-thiosulphate was formed. In making up the reagent methyl alcohol of technical grade, and in a pure anhydrous condition, was used. All salts used were of "AnalaR" quality, or, as in the case of rubidium chloride, were specially purified before use. The salts in the reagent tests were all chlorides. Rubidium chloride was recrystallised from distilled water until spectrographic examination showed the virtual removal of potassium from the sample.

Solutions containing decreasing amounts of potassium chloride were added in 0.1 ml quantities from a semi-microburette to the reagent in a test tube. Tests were commenced with a solution containing 50 mg K^+ per ml and successive dilutions were used until no precipitate was formed even on standing in a stoppered vessel for 12 hours. The concentration was then determined which gave a just perceptible precipitate in a few moments. The solution which behaved in this manner was one containing 3 mg K^+ per ml. It was found that standing the solutions for 12 hours was of no advantage as, far from a precipitate appearing in more dilute solutions, the precipitate obtained in the case of the 3 mg per ml solution actually disappeared when left for that time. As the test offers enough difficulties without having to purify and dry methyl alcohol it was decided to try the test with methyl alcohol of technical quality. The effect was to reduce the sensitivity as indicated in the table.

Tests were carried out in the same way using solutions of rubidium chloride and here the limit of perceptibility was reached with a solution containing 4 mg Rb^+ per ml which indicates that considering the higher atomic weight of rubidium compared with that of potassium, the reagent is a little more sensitive towards rubidium than to potassium.

The quantities of solvent and of reagents used to make up the methyl alcoholic solution of sodium cobalti-thiosulphate were then varied.

The conclusion reached was that if less methyl alcohol is used the sodium salt is thrown out of solution as a rather darker blue precipitate than that obtained with potassium. Also, when greater amounts of sodium thiosulphate and cobalt nitrate are added to the 10 ml of methyl alcohol the sensitivity of the reagent is less, presumably due to the greater amount of water now present. The effect of the volume of potassium chloride solution was next tried. It was found that

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the maximum sensitivity was obtained when only 0.1 ml of solution was added. With less than 0.1 ml the limit of perceptibility was lowered, while with greater amounts of solution added the test was again less sensitive as relatively more water had been added.

The reagent was tried with the chlorides of other alkali metals, with ammonium chloride and with the chlorides of the alkaline earth metals. It was found that none of these, excepting rubidium, gave a sky-blue precipitate, but that a white precipitate was obtained in the case of barium which on separation and analysis proved to be barium thiosulphate.

The sensitivity of the reagent for potassium was found to be unaffected by the addition of lithium or ammonium chlorides to the solutions of potassium chloride used in the tests up to a concentration of the cations 10 times that of the potassium ion.

2. Sodium-calcium ferrocyanide was suggested as a very sensitive reagent for the detection of potassium and ammonium by GASPAR Y ARNAL[2] and the reaction with the other alkali metal ions was investigated with a view to their separation by means of this reagent by DIAZ DE RADA AND GASPAR Y ARNAL[3]. No idea of the sensitivity of the reagent was given in either paper. It has been stated in abstracts that the reagent employed was calcium ferrocyanide, which certainly does give precipitates with the ions mentioned, but the reagent proposed by GASPAR was sodium-calcium ferrocyanide. This reagent is easier to prepare then calcium ferrocyanide of the required purity. Also the solutions of the reagent appear to be more stable than solutions of calcium ferrocyanide alone. The reagent originally used by GASPAR Y ARNAL was used in the present study and made up as follows: — a solution of 7 g of sodium ferrocyanide and 3.5 g of calcium chloride was made in a mixture of 80 ml of 96% ethyl alcohol and 95 ml of water.

The procedure in testing this reagent was to place one drop (0.025 ml) on a slide or watch glass and to place a drop (0.025 ml) of the solution under test beside it and allow the drops to mix. A very pale yellowish precipitate of a double ferrocyanide of calcium and the metal forming the precipitate was formed from the appropriate concentrations of the ions which react. In the case of solutions of potassium chloride the limit of perceptibility was reached with a solution containing 0.8 mg K^+ per ml. No solution weaker than this would give a precipitate on standing over night in a small stoppered tube.

Similar precipitates to that formed with potassium are formed with rubidium, caesium, and ammonium (from concentrated solutions only). No reaction occurs with solutions of lithium, strontium, barium or magnesium.

The sensitivity of the reagent for potassium was found to be unaltered by the presence of ten times the weight of lithium.

3. Sodium-uranyl chromate. This reagent was also proposed by GASPAR Y ARNAL[4] and was used exactly as the originator proposed. The reagent was

made up by dissolving 4.42 g of sodium chromate and 6.51 g of uranyl nitrate in water and making up to 100 ml, giving the equivalent of a 5% solution of uranyl chromate. It is to be noted that once again, abstracts call the reagent uranyl chromate, whereas GASPAR calls it sodium-uranyl chromate. The reagent gave a bright yellow precipitate of a double potassium uranyl chromate with potassium solutions of the right concentrations and similar precipitates with the other specified ions.

The testing was carried out as with sodium-calcium ferrocyanide. The limit of perceptibility was again reached with a solution of potassium chloride containing 0.8 mg of K^+ per ml. A precipitate could be obtained from a solution with a solution as little as 0.5 mg K^+ per ml if the solution was allowed to stand overnight in a small stoppered tube.

Precipitates of the same kind as that formed with potassium were found to be given by rubidium, and caesium, and as would be expected, a pale yellow precipitate of barium chromate was formed with barium. No precipitates were obtained with lithium, ammonium, calcium, strontium or magnesium.

The sensitivity of the reagent for potassium was unaffected by the presence of lithium or ammonium at ten times the concentration of the potassium.

The author wishes to express thanks to Mr. R. A. BELCHER of Birmingham University for suggesting the study and for his kindness and interest in the work at all stages.

SUMMARY

Sodium cobalti-thiosulphate, sodium-calcium ferrocyanide, and sodium-uranyl chromate have been investigated as proposed reagents for the detection of potassium. The dilution limits for the three reagents are respectively: $1 : 3.33 \cdot 10^2$, $1 : 1.25 \cdot 10^3$, and $1 : 1.25 \cdot 10^3$. Sensitivities are poor when compared with sodium cobalti-nitrite but it is possible that sodium cobalti-thiosulphate might prove of some use as a reagent for the detection of potassium in the presence of ammonium, or for the detection of rubidium in the absence of potassium, and that sodium-uranyl chromate might also be of use for detecting potassium in the presence of ammonium.

RÉSUMÉ

Trois réactifs du potassium ont été étudiés: le thiosulfate cobalticosodique, le ferrocyanure ed calcium et de sodium, le chromate d'uranyle et de sodium. Les limites de dilution obtenues avec ces 3 réactifs sont, respectivement: $1 : 3.33 \cdot 10^2$, $1 : 1.25 \cdot 10^3$ et $1 : 1.25 \cdot 10^3$. Les sensibilités, comparées à celle obtenue avec le nitrate cobalticosodique, sont faibles. Mais il est possible, au moyen de thiosulfate cobalticosodique, de déceler le potassium en présence d'ammonium, ou de déceler le rubidium en l'absence de potassium. Le chromate d'uranyle et de sodium permet également d'identifier le potassium en présence d'ammonium.

ZUSAMMENFASSUNG

Natriumcobaltithiosulfat, Natriumcalciumferrocyanid und Natriumuranylchromat wurden als vorgeschlagene Reagenzien zur Bestimmung von Kalium unter-

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sucht. Die Grenzkonzentrationen für diese drei Reagenzien sind 1 : $3.33 \cdot 10^2$ und 1 : $1.25 \cdot 10^3$, bzw. 1 : $1.25 \cdot 10^3$. Die Empfindlichkeit verglichen mit Natriumcobaltinitrit ist gering, aber es besteht die Möglichkeit, dass Natriumcobaltithiosulfat sich als Reagenz für die Bestimmung von Kalium bei Gegenwart von Ammonium oder für die Bestimmung von Rubidium bei Abwesenheit von Kalium von Nutzen erweist und dass ebenso Natriumuranylchromat von Nutzen sein könnte bei der Bestimmung von Kalium in Gegenwart von Ammonium.

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QUALITATIVE AND QUANTITATIVE ANALYSIS OF MIXTURES OF SULFONAMIDES IV

by

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Treatment of Group II

This group includes the water-insoluble sulfonamides, which are reviewed in Table II[63]. Since the number of these compounds is large, subdivisions are necessary and effected by the use of various solvents.

The mixture, from which the water-soluble compounds have previously been removed, is weighed and treated with five to seven parts of boiling water. The residue is filtered with suction and washed with a small quantity of boiling water. In this way there is obtained:

an aqueous solution . . . . Group IIa
  including sulfanilamide and sulfacetamide, also very small quantities of the compounds of group IIb.

a residue insoluble in hot water . . . . Group IIb
  including the remaining compounds (*cf.* Table II).

Treatment of Group IIa

This group is identical with group Ib (discussed in the preceding paper) with the exception of soluseptazine, which is not present here. The very small quantities of the compounds of group IIb that dissolve in boiling water do not interfere in the tests for the detection of sulfanilamide and sulfacetamide.

Marfanil, one of the compounds of less importance, mentioned at the end of our third paper, may also be present in this group.

Treatment of Group IIb

The residue is dried and weighed. Next it is treated with ten to fifteen parts of 10% sodium hydroxide. The remaining insoluble part is filtered with suction and washed with some alkali. In this way there is obtained:

a residue, insoluble in sodium hydroxide . . . . Group IIb1
  including irgafen, septazine and sulfaguanidine.
a solution in sodium hydroxide . . . . Group IIb2
  including the remaining compounds.

Treatment of Group IIb1

The precipitate is freed from adhering NaOH by pressing out on a porous plate. It contains irgafen in the form of its sodium salt (*cf.* our second paper), but the two other compounds are present in their "free" form. It is so easy to isolate in pure form the individual compounds of this group, that no previous tests are necessary to detect their identity. Therefore, the procedure for this isolation may follow immediately.

a) The squeezed substance is treated with thirty to fifty parts of cold distilled water, whilst the solid is divided as finely as possible by stirring and pressing with a glass rod: the sodium salt of irgafen is soluble in water, but dissolves at a low rate. After filtering with suction the residue is once again treated with the same amount of water. The two filtrates contain sodium-irgafen. Irgafen is precipitated upon acidifying with dilute acetic acid. It is filtered and recrystallized from ethyl alcohol and water. Melting point: 221-224°C[43]. For identification reactions we may refer to SCHALLENBERG[14] and ROSENTHALER[44].

b) The water-insoluble residue that was left after isolation of irgafen contains septazine and sulfaguanidine. The latter is separated by treatment of the mixture with dilute hydrochloric acid (7%). The insoluble septazine is filtered with suction and washed with a small amount of water. From the acid solution sulfaguanidine is obtained by careful neutralization with alkali or ammonia.

Filtration and recrystallization (from ethyl alcohol) as usual. The melting point is 185-193°C[43].

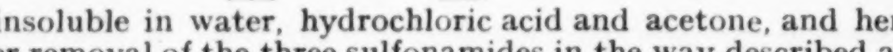
For some identification reactions we refer to HOFFMANN AND WILKENS[57], ROSENTHALER[44] and SCHALLENBERG[14].

c) Finally, septazine is isolated from the acid-insoluble residue by treatment with ten to fifteen parts of acetone. A possible residue is washed with a small amount of acetone. The solvent is evaporated on a water-bath and the residual septazine recrystallized from ethyl alcohol.

The melting point is 174-178°C[43].

Identification reactions are given by LAPIÈRE[2] and ROSENTHALER[58].

A substance of less importance, which may be found in this group, is rodilone



This compound is insoluble in water, hydrochloric acid and acetone, and hence is left as a residue after removal of the three sulfonamides in the way described above.

The melting point is recorded to be 293°C[2]. For identification reactions we also refer to LAPIÈRE[2].

Treatment of Group IIb2

To the alkaline solution of the compounds of this group dilute hydrochloric acid (1%) is carefully added. At the neutral point a precipitation of the water-insoluble compounds may occur, but may also fail to appear owing to retardation of crystallization. When continuing the addition of acid the precipitate of some compounds redissolves under formation of soluble hydrochlorides, while irgamid is converted into a hydrochloride that is but sparingly soluble in dilute hydrochloric acid, and succinylsulfathiazole does not dissolve since it cannot form a hydrochloride. Therefore, these two compounds are left as precipitates in the slightly acid solution. The phenomenon of retardation of crystallization must be taken into account however.

Hydrochloric acid is added to a slight excess only.

In this way there is obtained

a precipitate, insoluble in dilute hydrochloric acid .... Group IIb2 A
including irgamid and succinylsulfathiazole.

a slightly acid solution .... Group IIb2 B
including the sulfapyrimidine-compounds, sulfapyridine, sulfathiazole and sulfamethylthiazole.

The precipitate is filtered with suction and washed with a small amount of dilute HCl.

Treatment of Group IIb2A

a) Detection of irgamid.

The various tests have already been described in our second paper.

b) Detection of succinylsulfathiazole.

ba) Isolation of succinic acid.

10 mg of the substance are added to 4-5 ml of 20% sulfuric acid and the mixture boiled for 5 minutes. After cooling the main part of the sulfuric acid is neutralized by adding alkali until the reaction is only slightly acid.

The solution contains aminothiazole and succinic acid from succinylsulfathiazole and senecioic acid (2-methyl-propene-1-carboxylic acid-1) from irgamid. Use is now made of the difference in solubility in ether of the two acids. Succinic acid is much more soluble in water than in ether, whereas the reverse holds for senecioic acid. The theory of extraction (HOLLEMAN[59]) suggests the following procedure as a means of achieving a good separation in this case. First, the slightly acid aqueous solution is extracted with ether eight times, using every time an amount of nearly one eighth of the volume of the solution (extract a).

Next, the solution is extracted once again with twenty volumes of ether (extract b). a and b are collected separately.

Extract a contains nearly the total amount of senecioic acid, together with 20% of the succinic acid, whereas extract b contains 65% of the succinic acid in practically pure condition.

The last-named solution is dried with the aid of anhydrous sodium sulfate and evaporated to dryness in a water-bath. The residue is used in the following confirmatory reaction of succinic acid:
ba) Lead-salt (SCHOORL[60]). A drop of an aqueous solution of the residue, which must not be too concentrated, is heated to boiling on the edge of an object slide; a little piece of solid lead acetate is then immediately applied to the centre of the hot solution. The slide is allowed to cool without stirring or scratching the liquid. The crystals of lead succinate develop after some time (Fig. 19, 60×).

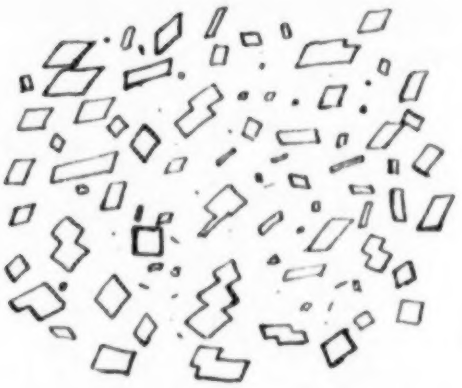


Fig. 19. Lead salt of succinic acid.

A few other reactions, which are less specific, are mentioned by BEHRENS AND KLEY[61].

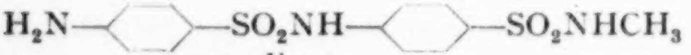
Isolation of the pure compounds is easy to perform when use is made of acetone as a solvent.
a. The mixture is extracted with five to ten parts of acetone. The residue, consisting chiefly of succinylsulfathiazole, is washed with a small amount of acetone, dried and recrystallized from methyl alcohol.

The melting point is 183-190°C[43].

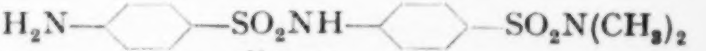
Two microchemical reactions are mentioned by SCHALLENBERG[14].
b. The acetone solution of the aforementioned extraction contains irgamid. It is evaporated to dryness in a water-bath and the crude irgamid recrystallized from methyl alcohol with much water.

For the melting point and additional reactions we may refer to our second paper.

Two compounds of less importance, neo-ulirone and ulirone, may also be found in this group



neo-ulirone



ulirone

No reactions are mentioned in the literature that may be of value in identifying these two sulfonamides.

Treatment of Group IIb2B

This group includes a number of very important sulfonamides. Most of them have already been mentioned in previous papers of this series in connection with the analysis of mixtures of the water-soluble sulfonamides.

a) Detection of sulfadiazine, sulfamerazine and sulfamezathine.

These three compounds are already discussed in the preceding paper.

b) Detection of elkosin.

ba) Reaction with potassium-mercuriciodide (HOFFMANN[62])

50-100 mg of the substance are dissolved in 5 ml of 30% acetic acid and to this solution 2-3 ml of a potassium-mercuriciodide-solution are added. Elkosin yields a white precipitation.

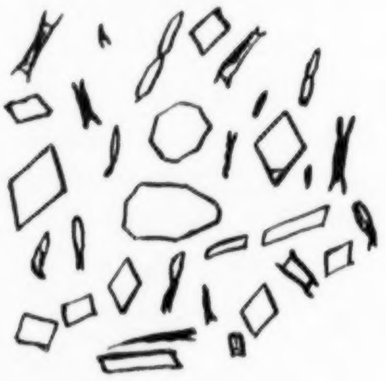


Fig. 20a. Sulfamethylthiazole from water.

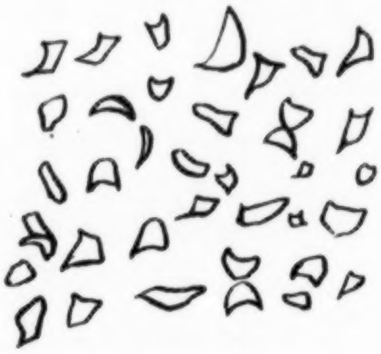


Fig. 20b. Sulfamethylthiazole from CH_3OH.

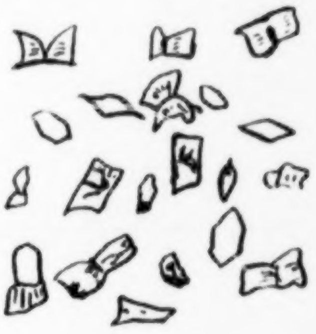


Fig. 20c. Sulfamethylthiazole from C_2H_5OH.

This reaction is completely specific for elkosin, and can without reserve be applied to a mixture of the compounds of this group.

In contrast to sulfamerazine and sulfamezathine, elkosin does not produce a coloration in the vanilline-reaction.

c) Detection of sulfathiazole and sulfapyridine.

All reactions are already discussed in the second and third paper, respectively.

d) Detection of sulfamethylthiazole.

No reactions are known that are specific for this compound and can be applied to establish its presence in a mixture. Detection is only possible, therefore, if use is made of chromatography.

Sulfamethylthiazole yields an insoluble yellow diazoniumchloride, just as sulfathiazole. But in the reactions with bichromate-sulfuric acid and with sodium nitrite it does not produce the colorations that are specific for sulfathiazole.

Isolation of the components of a mixture of these compounds seems to be a difficult task. The situation resembles that of group Ia2. Here, also, no general scheme can be given and use must be made of the solubilities of the compounds at the boiling points of some solvents, which are listed in Table IV and V. The latter include some additional data concerning sulfamethylthiazole and elkosin. Some crystalline forms of these compounds are shown in Fig. 20 and 21 (60×), which are additions to Fig. 13 to 17 already given. For the rest, we emphatically refer to the various remarks on the separations of group Ia2, given in the preceding paper, since these remarks are fully applicable to the group under consideration.

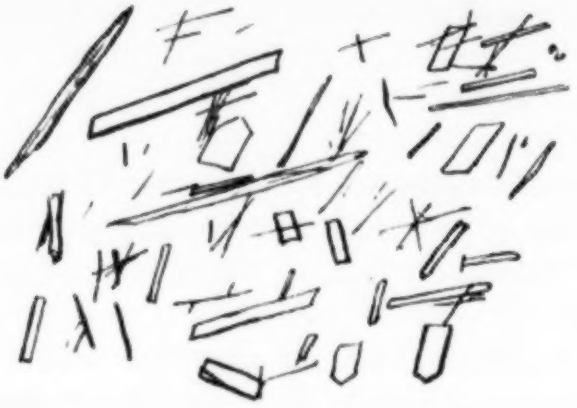


Fig. 21. Elkosin from water. All other solvents produce the same crystalline forms.

TABLE V

Compound	Water	CH_3OH	C_2H_5OH	Acetone/ water 1 : 1	Acetone/ water 1 : 3
Sulfamethylthiazole	—	++	++	++	+
Elkosin	— —	+	—	+	+

Compound	C_2H_5OH/ water 1 : 1	CH_3OH/ water 1 : 1	CH_3OH/ C_2H_5OH 1 : 1	CH_3OH/ C_2H_5OH/H_2O 1 : 1 : 2
Sulfamethylthiazole	++	+	++	++
Elkosin	++	+	—	++

For the melting points and identification reactions of the various compounds we also refer to the preceding paper; to the data given there the following ones may be added: sulfamethylthiazole: melting point 234 °C[44]; identification reaction: ROSENTHALER[44];
elkosin: melting point 240-242 °C[62]; identification reaction: HOFFMANN[62].

With the treatment of this group we brought to an end the discussion of our general separation scheme, based on "classical" methods and reactions. In many cases it proved to give satisfactory results, in others it fell short as a result of the similarity of the properties of some compounds, which prevented separation and identification. However, in these more difficult cases use can be made of chromatographic methods, which are excellently suitable for the separation of closely related compounds. They will be treated in the next paper.

In conclusion we shall now give the full accounts of the qualitative analysis of three mixtures of sulfonamides. They may serve as numerical examples to the general scheme, which necessarily was often treated above in a somewhat vague manner.

First analysis

In the preliminary examinations a positive test for sulfadiazine was obtained while the presence of one or two methylpyrimidine derivates could be concluded from the result of the vanilline reaction. The other preliminary tests turned out negative.

From the losses of weight observed during the search for the proper groups it was deduced that only compounds of group IIb2 B were present. Within this group, also, indications were exclusively obtained concerning the presence of sulfadiazine and of one or two sulfamethylpyrimidines. Isolation of the pure compounds was now accomplished as follows. 3.00 g of the dry pulverized mixture were gently boiled with 20 ml of 96% ethyl alcohol during a few minutes. While hot, the liquid was filtered with suction with the aid of a little Hirsch-funnel. The residue was washed with 2 ml of boiling alcohol. After drying its weight amounted to 1.43 g.

The clear, colourless filtrate yielded a precipitation of white crystals on cooling. They were filtered with suction; after drying on a water-bath: 1.1 g. The crystalline forms of this precipitation equalled those of Fig. 13b; from the presence of microcrystalline lumps, however, we concluded that, in addition to sulfamezathine, other compounds might still be present. After one recrystallization from ethyl alcohol the melting point was 168.5°C (corr.), which was much too low (pure sulfamezathine: 198°C). From this, and from the loss of weight observed, it appeared that too much alcohol had been used in the first extraction, whereby part of the other compound(s) had also been dissolved. To isolate sulfamezathine in a pure condition the low melting residue was again extracted with boiling alcohol. Since we were now concerned with the removal of the impurities, the extraction was carried out by boiling the solid with 0.5 ml of alcohol and filtering with suction at the boiling temperature. The remaining residue was treated in the same way. In all, the extraction was performed four times, each time using 0.5 ml of alcohol. The melting point had now risen to 194°C (corr.); the mixed melting point amounted to 195.5°C. The identity of sulfamezathine was thus confirmed. The melting point could still be raised somewhat by recrystallization twice from methyl alcohol: it then reached 196°C (corr.).

The aforementioned residue of 1.43 g, which might be composed of sulfadiazine and/or sulfamerazine, was boiled for half a minute with 20 ml of ethyl alcohol/water 1 : 1. The solution was filtered with suction at the boiling temperature.

From the filtrate a crop of colourless crystals was obtained on cooling: viewed under the microscope, the crystalline forms of sulfamerazine (Fig. 15b) and of sulfadiazine (Fig. 14b) were directly identified. We therefore concluded the presence of both compounds.

The residue of this second extraction should consist of sulfadiazine. Since in general this compound is but sparingly soluble in cold as well as in hot solvents, we tried to remove the admixtures with the aid of boiling acetone. This was effected by extracting the dried residue (weight: 0.81 g) twice with 15 ml of boiling acetone. After drying, the melting point of the remaining substance was 250°C; the mixed melting point was also 250°C. The identity of sulfadiazine was thus confirmed.

Finally filtering with suction was applied to the crystals that had separated on cooling the C_2H_5OH/H_2O extract, and that should contain sulfamerazine. The weight of this residue amounted to 0.43 g, the melting point was 211.5°C (pure sulfamerazine: 234°C). Purification was accomplished by extracting the solid twice with 2 ml of boiling acetone; the insoluble sulfadiazine was filtered and the filtrate evaporated to dryness, leaving a colourless residue. The latter was extracted again, using this time 1 ml of boiling acetone. After filtration and evaporation to dryness, the crude sulfamerazine was recrystallized from a mixture of ethyl and methyl alcohol (1:1). Now, the compound had a melting point of 231.5° and a mixed melting point of 232°, whereby its identity was confirmed.

Second analysis

According to the results of the preliminary examinations, sulfathiazole and sulfadiazine were present in the mixture. This was confirmed by the group-separations (only compounds of group IIb2 B) and the qualitative reactions within the proper group. The appearance of the original mixture at 60-fold magnification is shown in Fig. 1c[63].

Separation of the two compounds was effected by extracting 1.00 g of the mixture with 10 ml of boiling alcohol. The hot solution was rapidly filtered; upon cooling crystals were yielded as shown in Fig. 17b; sulfadiazine, however, was also present (Fig. 14b).

The residue of this extraction was washed with a little hot alcohol and dried. Weight 0.47 g. It should consist of sulfadiazine, but melted at 241°C, which is still somewhat too low. Extraction with boiling acetone was applied as described in the preceding analysis. Melting point 252°C, mixed melting point 251°C.

The crystals of sulfathiazole, separated on cooling the alcoholic extract, were filtered by suction and dried. 0.39 g was obtained, melting at 173°C (pure sulfathiazole 201°). Purification was accomplished by extracting the solid three times with 2 ml of *cold* acetone. The acetone was evaporated, the residue recrystallized from acetone. The melting point was then 199.5°C, the mixed melting point 200°C.

References p. 15.

Third analysis

In this case a self-made mixture was used, compounded of sulfathiazole (40%) and irgamid (60%). 2 g of this mixture were dissolved in 6 ml of 10% sodium hydroxide (as described in our second paper). Dilute hydrochloric acid (1%) was added with care till slightly acid reaction. The precipitation of irgamid hydrochloride was filtered by suction, washed with 3 ml of the acid and redissolved in dilute sodium hydroxide. From this solution irgamid was again obtained by precipitating with dilute acetic acid (3%). After filtering, washing with distilled water and drying, the weight of isolated irgamid amounted to 1.02 g. Melting point 174.5°C. After recrystallization from a mixture of methyl alcohol and much water, the compound melted at 176°C. Mixed melting point 175°C.

The acid solution of sulfathiazole hydrochloride was treated with sodium hydroxide and acetic acid as described in the second paper. 0.79 g of sulfathiazole was obtained, melting at 181°C, which is much too low. After recrystallization a few times from ethyl alcohol, the melting point was 185°C, the mixed melting point 186°C. Finally, the presence of a small quantity of irgamid causing the depression of the melting point could be established with the aid of paper chromatography.

These chromatographic methods will be the subject of the next paper.

SUMMARY

In this fourth paper the discussion of a general scheme for the qualitative analysis of mixtures of sulfonamides is brought to an end with the treatment of group II, including the water-insoluble sulfonamides (*cf.* Table II[63]). In addition, the analysis is described of three mixtures (sulfadiazine, sulfamerazine and sulfamezathine; sulfathiazole and sulfadiazine; sulfathiazole and irgamid), which serves as a numerical example to the general scheme.

RÉSUMÉ

Dans ce quatrième mémoire, on achève la discussion d'une méthode générale d'analyse qualitative de mélanges de sulfamidés (traitement du groupe II, comprenant les sulfamidés insolubles dans l'eau) (*cf.* Tableau II[63]). Comme supplément, on décrit l'analyse de trois mélanges (sulfadiazine, sulfamérazine et sulfamézathine; sulfathiazole et sulfadiazine; sulfathiazole et irgamid), servant d'exemple pratique du schéma général.

ZUSAMMENFASSUNG

In dieser vierten Mitteilung wird die Besprechung einer allgemeinen Methode für die qualitative Analyse von Mischungen wichtiger Sulfonamiden beendet mit der Behandlung der Gruppe II welche die wasser-unlösliche Sulfonamiden umfaszt (vgl. Tabelle II[63]). Im Anschlusz wird die Analyse beschrieben von drei Mischungen (Sulfadiazin, Sulfamerazin und Sulfamezathin; Sulfathiazol und Sulfadiazin; Sulfathiazol und Irgamid), welche fungiert als numerisches Beispiel für das allgemeine Schema.

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A WET-COMBUSTION METHOD FOR THE DETERMINATION OF CHLORINE IN COALS

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The standard method for the determination of chlorine in coals depends on incineration of the sample with Eschka mixture at 500° ± 25°C for 24 h[1]. The chloride ion is finally determined by the Volhard titration. Several years ago Panel 1 (Sampling, Analysis and Testing) of the British Coke Research Association initiated an investigation with the object of reducing considerably the time involved in this process. The same organisation had already recommended an alternative method[2,3], requiring a total time of about 20 min for a single sample, but since this method necessitated the use of a high temperature furnace, it was considered desirable to recommend an alternative method for which more readily available apparatus could be used. As a result of this investigation, which was spread over four years, and in which many laboratories cooperated, B.C.R.A. Panel[4] finally recommended a modified Eschka method which required an incineration period of only 1 h.

During the course of this work it was considered desirable to check the accuracy of the method not only against the standard method, but against independent methods of analysis. Only two such methods for the determination of chlorine in coal have been described: the high temperature combustion method[3] and the bomb method[5]. It was not convenient to use the latter method, because the bomb is generally in constant use for the determination of calorific values. Accordingly, the present author was asked to explore the possibility of applying one of the many classical methods available for the determination of halogens in organic compounds to coals. The most attractive of these appeared to be the method of wet combustion, and after suitable modification this was applied successfully to the determination of chlorine in coals.

The wet-combustion method was originally developed as a means of obtaining an independent check on the chlorine content of coals, but it has certain features which may make it useful as a routine method of analysis.

(1) It requires only simple apparatus.
(2) It is rapid.
(3) No filtration is necessary.
(4) It is suitable for batch analysis.
(5) The results are unaffected by a contaminated laboratory atmosphere.

Although a large amount of potassium dichromate is consumed per determination, the actual cost works out about the same as the B.C.R.A. method and considerably less than the B.S. method.

Development of the method

Although the amount of sample to be taken was necessarily restricted to the macro range (to avoid sampling errors) the amount of chlorine to be determined (rarely as much as 1 per cent.) lay in the micro range. Accordingly, only micro methods for the determination of chlorine were considered. Of these the VIEBÖCK procedure[6] was chosen for adaption because some considerable experience with it had been gained in the microanalysis of organic compounds.

The apparatus consists essentially of a decomposition flask and an absorption system. This general form was retained with some modification. Although the amount of chlorine to be absorbed was of the same order as in the microanalysis of organic compounds, the amount of sample to be decomposed was at least one hundred times as great. A much larger decomposition flask was therefore used. In the initial experiments the original VIEBÖCK absorption system was used, but later, a more compact system described by NUTTEN[7] was incorporated. The electrically-heated aluminium block described by the same author could probably be adapted for batch analysis. It was not tried in the present investigation since the determinations were done singly.

The method is based on decomposition with sulphuric acid and potassium dichromate in the presence of silver sulphate. The products of decomposition are swept into neutral hydrogen peroxide by means of a current of air. The hydrochloric acid formed is determined alkalimetrically. In certain cases other acid-forming gases are retained by the absorbent, *e.g.* nitrogen oxides when nitro-groups are present, and a control titration is recommended which is specific for halide ions. A solution of mercuric oxycyanide is added to the neutralized solution

$$\mathrm{Hg(OH)CN + NaCl \rightarrow HgCl.CN + NaOH}$$

and the increase in alkalinity is equivalent to the original amount of chloride ion. This liberated alkali is titrated with standard sulphuric acid.

When coal was decomposed, it was found that fumes of sulphuric acid or sulphur dioxide passed into the absorber and the mercuric oxycyanide method had to be used in every case. Since the amount of sample taken (0.5 g) was over one hundred times that used by VIEBÖCK it became necessary to establish the conditions under which chlorine could be liberated quantitatively from coal.

Without describing in detail the many trials made, it will suffice to say that the amounts of sulphuric acid and potassium dichromate and their ratios, the time of digestion and the temperature of reaction were varied. Potassium sulphate was also added in an attempt to overcome the passage of acid fumes into the absorbent. Some of these conditions gave low results, but it was established that the most important factors were the minimum amounts of sulphuric acid and potassium dichromate which could be used and the temperature of decomposition.

The presence of silver ions are essential in the process. Silver chloride is formed intermediately and when decomposed by sulphuric acid and dichromate does not form chromyl chloride. Accordingly, the ratio of silver sulphate to sulphuric acid should not be important provided that there is sufficient silver ion available to combine with the total amount of chloride present. Tests were carried out in which the silver sulphate was reduced to the *amount* present in the original VIEBÖCK method although the sulphuric acid had been increased almost fifteen-fold. No chromyl chloride formed under these conditions and the results were unaffected. This modification effected considerable saving in silver sulphate although as a matter of routine it was recovered from the residue.

In the original VIEBÖCK method digestion is continued until the compound is decomposed completely. This was not found to be necessary in the case of coals, probably because the chlorine is present completely in an inorganic form. When 0.5 g of coal was decomposed with 40 ml of sulphuric acid containing 0.15 g of silver sulphate and 25 g of potassium dichromate, at 150 °C no further quantities of chlorine were evolved after digesting for about 1 h. The total time for the digestion was standardised for a period of 90 min. Appreciable quantities of undecomposed organic material remain at this stage but need cause no alarm for the reasons already stated.

The above conditions were established by working with a coal supplied by the Midland Coke Research Station, the chlorine content of which (0.48 per cent.) had been established by several laboratories. This coal is represented as Coal 9 in Table 1 and is the mean of about 20 determinations carried out after the final conditions had been established. Coals 1 to 6 in the Table were determined as unknowns, and the results by other methods were only disclosed after the figures obtained by the wet-combustion method had been submitted to B.C.R.A. Panel 1. Only single determinations were purposely carried out on these coals to avoid selection or the inclusion of mean values. Several determinations were carried out using Coal 8 to ascertain whether or not difficulties were likely to arise with a coal containing an abnormal amount of chlorine. These results are summarised in Table I.

References p. 21.

TABLE I

COMPARISON OF RESULTS BY THE WET-COMBUSTION METHOD WITH OTHER METHODS
(expressed as percentage on the dry coal)

Coal	1	2	3	4	5	6	7	8	9
B.C.R.A. Method*	0.06	0.57	0.47	0.67	0.39	0.14	0.04	0.86	0.48
High Combustion Temperature Method**	0.05	0.59	—	0.66	0.39	0.15	0.05	0.88	—
Wet-Combustion Method	0.06	0.55	0.44	0.65	0.40	0.16	0.04	0.87	0.48

* Incineration with Eschka mixture followed by Volhard titration.
** Combustion in a tube at a high temperature and absorption of chlorine in hydrogen peroxide.

Method for the determination of chlorine in coal by wet-combustion

Apparatus

The final form of the apparatus used and its dimensions which are not critical are shown in Fig. 1. The discs in the absorber have a hole in the centre through which passes the capillary delivery tube. The holes are of such a size that an airlock is formed and maintained when the absorption vessel is filled and air is passed through. Filling is effected through the vertical side-arm. This is stoppered during a determination. The large-sized flask is essential because the mixture froths during the decomposition.

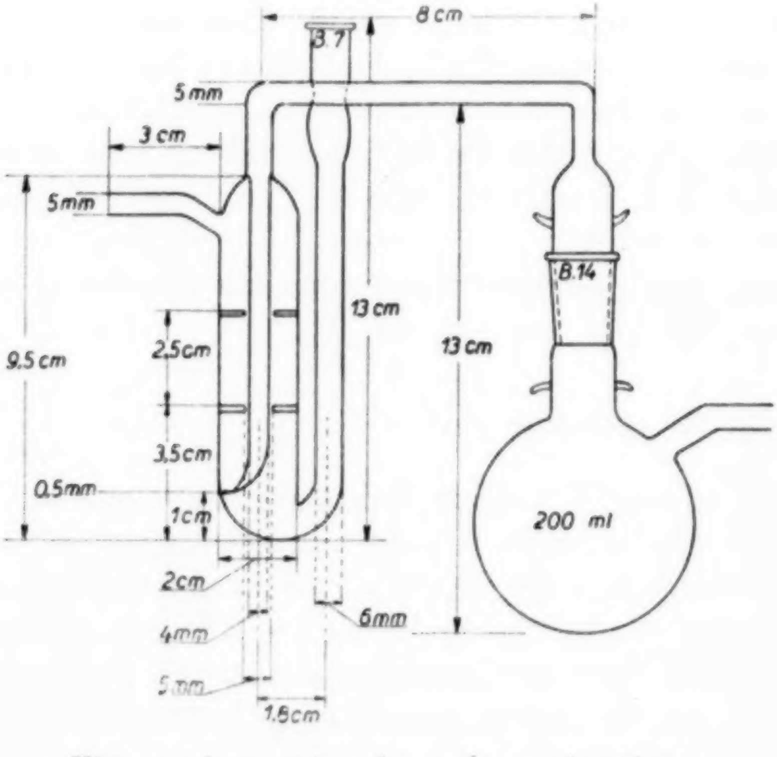

Fig. 1. Apparatus for wet-combustion.

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Reagents

Concentrated sulphuric acid containing 1.5 g of silver sulphate per 400 ml
Potassium dichromate (recrystallised)
Hydrogen peroxide (3%)
Saturated mercuric oxycyanide solution
0.1 *N* sodium hydroxide
0.0141 *N* sulphuric acid (1 ml = 0.1 per cent. Cl on 0.5 g sample)
Screened indicator (0.125 g methyl red and 0.083 g methylene blue dissolved in 100 ml of 95% ethanol).

Procedure

Transfer 10 ml of 3 per cent. hydrogen peroxide to the absorber and distribute it equally throughout the three compartments. Transfer 0.5 g of coal and 25 g of potassium dichromate (which may be measured from a graduated tube) to the digestion flask and mix well. Add 40 ml of concentrated sulphuric acid containing silver sulphate, attach a soda-lime guard tube to the side-arm of the flask and draw air through the apparatus at a rate of 2 to 3 bubbles per sec. Allow the reaction to proceed for 20 min. The heat of reaction is sufficient to maintain the required temperature during this period. Immerse the flask in an oil bath maintained at 145°-155°C and allow the decomposition to proceed for a further 70 min. Disconnect the absorber and pour the contents into a 100 ml conical flask through the side-arm. Wash by introducing water through the vertical filling tube and through the larger ground joint. Add 3 or 4 drops of indicator and add 0.1 *N* sodium hydroxide until the indicator just turns green. Adjust the solution to the neutral point by adding 0.0141 *N* sulphuric acid. Add 10 ml of saturated mercuric oxycyanide solution neutralised just before use with the standard sulphuric acid. Titrate the liberated alkali with the standard sulphuric acid using a macroburette.

Deduct a blank value obtained under the same conditions of digestion.

1 ml of 0.0141 H_2SO_4 = 0.1 per cent. Cl.

Standardisation of the sulphuric acid

Transfer 20 ml of 0.01 *N* sodium hydroxide (standardised against potassium bi-iodate) to a 100 ml conical flask. Add 10 ml of neutralised saturated mercuric oxycyanide solution and a few drops of screened indicator. Titrate with the sulphuric acid to the neutral point. Adjust the strength of the stock solution to 0.0141 *N* according to the titre obtained and re-check the standardisation.

Thanks are due to the British Coke Research Association for permission to quote the analyses given in Table I.

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SUMMARY

Chlorine in coals can be determined by wet-combustion with sulphuric acid in the presence of potassium dichromate and silver sulphate. The liberated chlorine is absorbed in hydrogen peroxide and after treatment with mercuric oxycyanide is determined acidimetrically. The method is simple, fairly rapid and should be suitable for multiplicate analysis. The results agree well with those given by two independent methods of analysis, *i.e.* incineration with Eschka mixture followed by the Volhard titration, and the high temperature combustion method.

RÉSUMÉ

Le chlore dans les charbons peut être dosé par combustion par voie humide au moyen d'acide sulfurique en présence de dichromate de potassium et de sulfate d'argent. Le chlore libéré est absorbé dans le peroxyde d'hydrogène; après traitement avec l'oxycyanure de mercure, il est dosé par acidimétrie.

La méthode est simple, relativement rapide et convient à des dosages en séries.

Ces résultats correspondent bien à ceux obtenus par 2 méthodes différentes:

1) incinération avec le mélange d'Eschka et titration par la méthode de Volhard;

2) méthode de combustion à haute température.

ZUSAMMENFASSUNG

Chlor in Kohle kann durch die Verbrennung auf nassem Wege mit Schwefelsäure in der Gegenwart von Kaliumdichromat und Silbersulfat bestimmt werden. Das freigesetzte Chlor wird in Wasserstoffsuperoxyd absorbiert und nach der Behandlung mit Quecksilberoxycyanid acidimetrisch bestimmt. Die Methode ist einfach, geht ziemlich schnell und würde für Reihenunterschungen passend sein. Die Ergebnisse stimmen gut überein mit denen von zwei unabhängigen Analysenmethoden, nämlich der Verbrennung mit Eschka-Mischung und nachfolgender Titration nach Volhard und der Verbrennung bei hoher Temperatur.

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ISOLEMENT DU TECHNETIUM

par

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Le technetium artificiel est le plus souvent préparé par bombardement du molybdène par particules convenables. D'autre part il prend naissance au cours de la fission de l'uranium.

La séparation de l'élément des produits irradiés est délicate. Lorsque le technetium est formé à partir du molybdène, il faut éliminer ce dernier au moyen de réactifs organiques (oxyquinoléine[1], α-benzoïnoxime) ou du nitrate d'argent[2], ou bien distiller en milieu sulfurique[3] ou perchlorique[4] l'oxyde Tc_2O_7 plus volatil que l'oxyde molybdique. Il faut ensuite pour isoler l'élément, ajouter un entraîneur, généralement le rhénium dont on précipite un sel peu soluble qui entraîne le sel correspondant de technetium. Les sulfures de rhénium et le perrhénate de tétraphénylarsonium ont été utilisés[1,5].

Nous avons essayé de mettre au point une méthode de séparation quantitative du technetium pur, sans recourir à des précipitations ou à l'addition d'entraîneurs. Précédemment l'une de nous a pu séparer des traces de rhénium par extraction du perrhénate de tétraphénylarsonium dans le chloroforme[6] et a constaté que les éléments usuels de la 7ème colonne de la classification périodique, à leur valence supérieure, se comportent qualitativement comme le rhénium en présence de chloroforme et de cations du type $(C_6H_5)_4\,As^+$.

Nous avons donc étudié l'extraction du technetium à l'état de pertechnétate de tétraphénylarsonium.

La source de technetium fournie par le Commissariat à l'Energie Atomique était de l'oxyde molybdique MoO_3 (en général 10 g) irradié par neutrons à la pile de Châtillon. Les réactions nucléaires sont les suivantes:

$$ {}^{98}_{42}\mathrm{Mo} \xrightarrow[\eta,\,\gamma]{} {}^{99}_{42}\mathrm{Mo} \xrightarrow[\beta^-]{67\mathrm{h}} {}^{99}_{43}\mathrm{Tc} \xrightarrow[\gamma]{6\mathrm{h}} {}^{99}_{43}\mathrm{Tc} \xrightarrow[\beta^-]{3\cdot 10^5\ \mathrm{ans}} {}^{99}_{44}\mathrm{Ru}\ \text{stable} $$

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Le technetium 6h se désintègre en donnant Tc $3 \cdot 10^5$ ans et un rayonnement γ de 0.14 Mev partiellement converti en électrons de 0.12 Mev.

Ce rayonnement étant très absorbable nous avons suivi l'activité de l'élément au cours des traitements chimiques à l'aide d'un compteur cloche C.E.A. à paroi de mica de 4 mg/cm².

PRÉPARATION D'UNE SOLUTION ÉTALON DE TECHNETIUM

Pour étudier quantitativement l'extraction il était nécessaire de préparer une solution de technetium actif pur débarrassé de tout élément capable de donner un sel de tétraphénylarsonium peu soluble dans l'eau ou extractible par le chloroforme, et autant que possible de toute activité étrangère, ceci pour la simplicité des mesures. Pour cela, de notre source de molybdène, il fallait isoler au moins une partie du technetium présent.

Nous avons essayé les méthodes de distillation de l'oxyde Tc_2O_7 mais préféré préparer la solution étalon en effectuant, à partir du produit irradié mis en solution, une extraction qualitative du pertechnetate de tétraphénylarsonium par le chloroforme. La difficulté consistait à réaliser une extraction suffisante en utilisant une concentration de réactif assez faible ($5 \cdot 10^{-5}$ *M*) pour que la quantité de ce réactif extrait avec l'élément soit négligeable au cours de l'étude quantitative ultérieure. Nous avons finalement adopté le mode opératoire décrit plus loin p. 26 - paragraphe a).

L'extraction étant effectuée en milieu alcalin, le molybdène demeure dans la phase aqueuse[6].

L'extrait chloroformique après séchage est lavé deux fois à l'eau distillée. D'après les mesures la deuxième eau de lavage contient la majeure partie du technetium séparé. La période de ce technetium a été suivie plusieurs jours et trouvée de 6 heures à 1% près. Des mesures d'absorption ont confirmé l'identité du rayonnement.

ÉTUDE QUANTITATIVE DE L'EXTRACTION

Comme dans le cas du rhénium, l'extraction du technetium heptavalent par le chlorure de tétraphénylarsonium et le chloroforme doit être déterminée par les constantes de deux équilibres, l'un concernant le partage du réactif:

$$(C_6H_5)_4\ As^+ + Cl^- \rightleftarrows (C_6H_5)_4\ AsCl_{CHCl_3}$$

$$\text{avec} \quad \frac{[(C_6H_5)_4\ As^+]\ [Cl^-]}{[(C_6H_5)_4\ AsCl]_{CHCl_3}} = K$$

que nous avons précédemment déterminé $K \sim 5 \cdot 10^{-3}$.

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L'autre relatif à l'extraction du technetium:

$$(C_6H_5)_4\ As^+ + TcO_4^- \rightleftarrows (C_6H_5)_4\ AsTcO_{4\,CHCl_3}$$

$$\text{avec}\ \frac{[(C_6H_5)_4\ As^+]\ [TcO_4^-]}{[(C_6H_5)_4\ AsTcO_4]_{CHCl_3}} = K'$$

Théoriquement cette constante K' est la seule inconnue à déterminer pour résoudre le problème général de l'extraction. En effet, supposons égaux les volumes des phases aqueuses et chloroformique et définissons le coefficient de partage apparent:

$$D = \frac{[(C_6H_5)_4\ AsTcO_4]_{CHCl_3}}{[TcO_4^-]_{eau}}$$

rapport des concentrations du technetium dans les deux phases données directement par les dosages radiométriques.

$$\text{On a}\quad D = \frac{1}{K'}\ [(C_6H_5)_4\ As^+].$$

Etant sûres d'utiliser toujours un grand excès de réactif par rapport aux traces de technetium nous négligerons le réactif combiné par rapport à sa concentration totale. Les formules donnant le coefficient de partage apparent vont être ainsi indépendantes de la quantité de technetium présent ce qui simplifie puisque nous ne la connaissons pas en valeur absolue.

Considérons seulement les deux cas particuliers simples que nous avons étudiés expérimentalement:

1. il n'y a pas d'ions Cl^- autres que ceux apportés par le réactif.

D'après la valeur de K, si la concentration du chlorure de tétraphénylarsonium est inférieure à $5 \cdot 10^{-4}$, moins de 10% de ce sel passe dans le chloroforme au moment de l'extraction. On confond donc la concentration du réactif à l'équilibre dans l'eau $[(C_6H_5)_4\ As^+]$ avec la concentration totale c. On a donc simplement $D = \frac{c}{K'}$.

Dans ces conditions on tire immédiatement K' de la détermination de D.

2. il y a dans la solution une quantité d'ions Cl^- telle que le réactif est pratiquement totalement extrait à l'état de $(C_6H_5)_4AsCl$.

Ceci se produit à 10% près lorsque $[Cl^-] \geqslant 5 \cdot 10^{-2}$. On a alors $D = \frac{K}{K'}\frac{c}{[Cl^-]}$ formule également simple qui permet le calcul de K', K étant connu ainsi que c et $[Cl^-]$.

D'après ce qui précède il suffisait donc en principe de déterminer quelques valeurs de coefficient de partage apparent pour calculer la valeur de la constante K'. Mais étant donné les traces infimes d'élément noyées dans une grande quantité de matière nous pouvions craindre de ne pas atteindre par agitation l'équilibre d'extraction et surtout d'être gênés par des phénomènes d'adsorption ou d'oxydoréduction.

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RÉSULTATS

En suivant le mode opératoire exposé plus loin deux séries d'essais de détermination du coefficient de partage apparent ont été effectuées:

1ère série: sans chlorure de sodium

Nous avons fait varier la concentration du chlorure de tétraphénylarsonium de $0.5 \cdot 10^{-5}$ à 10^{-4} *M*.

La valeur de K′ calculée d'après les valeurs expérimentales du coefficient de partage n'est pas constante. D'autre part l'augmentation du temps d'agitation des deux phases provoque une diminution du coefficient de partage. Les résultats ne s'améliorent pas si on ajoute quelques γ de perrhénate de potassium comme entraîneur, quantité assez faible pour ne pas consommer sensiblement le réactif, ou bien si on réalise l'extraction en milieu acide (SO_4H_2 0.1 *N*).

Remarque. Aux erreurs expérimentales près nous n'avons pas observé de pertes en technetium au cours des bilans: celui-ci dans nos conditions opératoires ne s'adsorbe donc pas sur les filtres ou sur les parois de verre des récipients.

Les coefficients de partage trouvés étant trop faibles, nous avons pensé qu'il se produisait au cours de l'extraction, soit une destruction presque totale du réactif, soit une légère réduction du technetium heptavalent. La première hypothèse est peu vraisemblable car nous savons par des expériences précédentes que le chlorure de tétraphénylarsonium reste stable en présence de chloroforme. La deuxième l'est davantage, car si l'extraction est effectuée en présence d'un excès d'oxydant (persulfate, cérium(IV), eau oxygénée) on constate une augmentation des coefficients de partage; cependant ceux-ci ne permettent toujours pas de calculer pour *K′* une valeur constante.

La purification du chloroforme utilisé par agitation avec une solution de carbonate de sodium suivie d'une distillation et d'une nouvelle agitation avec du cérium(IV) acide, n'a pas modifié les résultats.

Le même phénomène de réduction est observé lorsqu'on extrait des solutions diluées de perrhénate de potassium par le chloroforme et le chlorure de tétraphénylarsonium.

L'essai suivant permet de penser que le réactif, ou une impureté qu'il contient, est capable de réduire, au moins partiellement, la valence(VII) des éléments de la 7ème colonne de la classification périodique: nous avons laissé une nuit au bain de sable doux une solution $5 \cdot 10^{-5}$ *M* en perchlorate de potassium et 10^{-4} *M* en chlorure de tétraphénylarsonium, ayant choisi ces faibles concentrations pour éviter la précipitation du perchlorate organique. Le lendemain le dosage du chlorure dans la solution réduite au dixième de son volume initial a montré que 30% des ions ClO_4^- avaient été réduits en chlorure.

Or, la valence (VII) du chlore est plus difficile à réduire que celle du technetium ou du rhénium.

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Remarque. La réduction d'une faible fraction du technetium(VII) présent suffit pour expliquer la diminution observée du coefficient de partage. En effet pour $[(C_6H_5)_4AsCl] = 2 \cdot 10^{-5}$ *M* nous trouvons D = 10 (au lieu de 65 comme nous verrons plus loin), ce qui se justifie par la réduction de moins de 10% du technetium total, la forme réduite demeurant en phase aqueuse. Si nous faisons une nouvelle extraction de cette phase aqueuse sans ajouter de nouveau réactif nous ne trouvons plus 10 comme coefficient de partage mais 2, ce qui confirme l'hypothèse de la réduction puisque nous savons que la concentration de Tc est sans influence.

2ème série d'essais: avec chlorure de sodium

Pour une concentration $[(C_6H_5)_4 AsCl] = 2 \cdot 10^{-5}$ *M* nous avons fait varier la concentration des ions Cl^- de 10^{-2} à $2 \cdot 10^{-1}$ *M*.

Les valeurs du coefficient de partage apparent pour les valeurs de $[Cl^-]$ comprises entre $5 \cdot 10^{-2}$ et $2 \cdot 10^{-1}$ ont alors vérifié la relation $D = \frac{K}{K'} \frac{c}{[Cl^-]}$ et permis ainsi de calculer une valeur de K' à peu près constante $K' \sim 3 \cdot 10^{-7}$.

Tout se passe comme si en présence de chlorure, le technetium (VII) n'était pas réduit et nous atteignons dans ce cas une valeur approchée de la constante d'équilibre.

D'après la valeur de celle-ci, il est possible de réaliser une extraction quantitative de l'élément en présence de chlorure (si $[Cl^-] = 10^{-1}$ $D > 100$ pour $c \sim 10^{-3}$ *M*) mais il ne faut pas oublier que dans ce cas la plus grande partie du réactif utilisé accompagne le technetium extrait, la présence de chlorure déplaçant l'équilibre d'extraction de ce réactif.

Mode opératoire

a. Préparation d'une solution de Tc(VII) pur.

Réactifs:
Soude 10 *N* R.P.
Persulfate de sodium R.P.
Bicarbonate de sodium R.P.
Chlorure de tétraphénylarsonium pur, solution 10^{-3} *M*.
Chloroforme purifié.
Sulfate de sodium anhydre R.P.

10 g d'oxyde molybdique MoO_3 irradié sont dissous dans le minimum de soude 10 *N* en présence de 20 ml d'eau et de 0.1 g de persulfate. Chauffer pour accélérer la dissolution. Ajuster le pH entre 10 et 11 en ajoutant du bicarbonate de sodium si le pH est trop élevé et amener la solution à 50 ml. Rendre cette solution $5 \cdot 10^{-5}$ *M* en chlorure de tétraphénylarsonium par addition de 2.5 ml de solution 10^{-3} *M*. Agiter 5 minutes avec 50 ml de chloroforme fraîchement purifié (D ∿ 15). Filtrer sur filtre mouillé de chloroforme et sécher sur sulfate de sodium. Filtrer à nouveau sur filtre mouillé de chloroforme et laver 5 min par agitation avec 30 ml d'eau distillée légèrement alcalinisée par la soude diluée (pH 10 à 11). Après nouvelle

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filtration laver une deuxième fois la phase chloroformique 15 min avec de l'eau distillée. La phase aqueuse de lavage contient alors la plus grande partie du technetium extrait à l'état pur et exempt de réactif. Il est bon de contrôler la première eau de lavage et le chloroforme restant. En général on perd en tout au plus 15% du technetium extrait.

Remarques. 1. Pour éviter cette perte on peut supprimer le lavage et se contenter de sécher et filtrer deux fois la phase chloroformique extraite. On distille le chloroforme et reprend par l'eau chaude. La quantité de réactif extraite, plus grande que précédemment, est de l'ordre d'une dizaine de γ.

2. On peut utiliser une plus grande quantité de réactif pour l'extraction ($c > 5 \cdot 10^{-5}\ M$) mais la quantité présente à côté du technetium à la fin du traitement augmente aussi.

b. Etude expérimentale de l'extraction.

Il est nécessaire que tout le technetium contenu dans la solution étalon soit à la valence(VII). Pour plus de sûreté nous avons toujours fait bouillir cette solution en milieu ammoniacal avec quelques gouttes d'eau oxygénée avant de faire les prises d'essai.

Plusieurs prises d'essai de 0.5 ou 1 ml ont été ensuite évaporées au bain-marie sur verre de montre de 3 cm de diamètre et leurs activités mesurées en fonction du temps a permis de construire la droite de décroissance $\log A = f(t)$ et de confirmer la valeur de la période. Puis on a procédé aux essais quantitatifs de la manière suivante:

Un volume convenable (5 à 10 ml d'après l'activité de la solution étalon) est prélevé et additionné de 0.5 ml d'eau oxygénée 100 volumes ou de 0.1 g de persulfate puis des volumes d'eau et de solution titrée de réactif nécessaires pour obtenir par exemple 15 ml de solution $2 \cdot 10^{-5}\ M$ en $(C_6H_5)_4AsCl$. On agite cette solution avec 15 ml de chloroforme pendant un temps qui a varié de 5 min à 1 heure. Les deux phases sont ensuite filtrées sur filtre mouillé du solvant correspondant et évaporées à 0.5 ml dans de petites capsules de verre Pyrex, puis transvasées sur verre de montre et évaporées à sec. Dans le cas où les solutions ne contiennent que le technetium et le réactif, l'activité présente sur les verres de montre peut être directement comparée à l'activité mesurée par évaporation d'une partie aliquote de la solution étalon, la quantité de matière étant au maximum de 0.1 mg; aux erreurs d'expérience près la somme des activités des deux phases correspond bien au technetium introduit initialement.

Mais si l'extraction a été réalisée en présence de persulfate ou de chlorure de sodium, ces sels demeurés en phase aqueuse cristallisent à l'évaporation. Il faut alors comparer le résidu sur verre de montre à un mélange préparé par évaporation de la même quantité de sel de sodium en présence d'un volume connu de solution étalon active, ceci pour déterminer le facteur de réduction dû à l'absorption du rayonnement dans la matière.

Nous avons écrit plus haut que quelques essais avaient été effectués en milieu HCl ou SO_4H_2. Dans ce cas il est impossible après extraction de procéder directe-

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ment à l'évaporation de la phase aqueuse. En effet l'évaporation au bain-marie en milieu acide provoque des pertes importantes en technetium probablement distillé à l'état d'acide TcO_4H. Pratiquement on extrait donc une deuxième fois après une nouvelle oxydation la phase aqueuse par le chloroforme en présence d'une quantité de réactif telle que cette extraction soit suffisamment quantitative ($c = 10^{-4}\ M$) et on mesure l'activité contenue dans la phase chloroformique.

EXTRACTION DU TECHNETIUM FORMÉ PAR FISSION DE L'URANIUM

L'oxyde d'uranium irradié par neutrons contient tous les produits de fission. Seul l'iode doit être séparé car il est extractible par le chloroforme et certaines de ses valences donnent lieu à un équilibre d'extraction en présence de chlorure de tétraphénylarsonium et de chloroforme. Sans précautions particulières le rayonnement dû à l'iode contamine plus ou moins le technetium extrait.

L'oxyde UO_3 est dissous dans l'acide sulfurique dilué en présence de quelques γ d'iodure, on ajoute du persulfate et extrait l'iode libéré avec du toluène. La solution est ensuite portée à l'ébullition pour chasser les dernières traces d'iode, puis neutralisée avec du carbonate d'ammonium. Après une nouvelle ébullition avec du persulfate la solution est prête pour l'extraction du technetium qui est réalisée comme précédemment. Les autres produits de fission ne semblent pas contaminer le technetium extrait.

RÉSUMÉ

Etude quantitative de l'extraction du technetium par le chloroforme à l'état de pertechnetate de tétraphénylarsonium. Application à la séparation de l'élément produit artificiellement à partir du molybdène ou de l'uranium.

SUMMARY

The extraction of technetium, in the form of tetraphenylarsonium pertechnate, by chloroform has been studied. This method has been used to separate the element artificially produced from molybdenum or uranium.

ZUSAMMENFASSUNG

Die Extraktion von Technetium als Tetraphenylarsonium-Pertechnetat mit Hilfe von Chloroform wurde untersucht. Diese Methode wurde angewendet um das künstlich aus Molybdän oder Uran hergestellte Element abzutrennen.

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NOTES SUR LES MÉTHODES DE DOSAGE DU TRYPTOPHANE

par

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La teneur en tryptophane des protéines peut être déterminée principalement par deux types de méthodes: les méthodes biologiques et les méthodes chimiques. Ces méthodes ne nécessitent généralement pas la séparation préalable du tryptophane des autres acides aminés. Si la séparation était désirée, elle pourrait être obtenue soit par une précipitation du tryptophane par une solution de sulfate de mercure en présence d'acide sulfurique, soit par des méthodes chromatographiques en employant entre autre une colonne remplie d'amidon d'après MOORE ET STEIN[43] ou contenant du carbonate de zinc TURBA ET VON SCHRADER-BEIELSTEIN[71].

Les méthodes biologiques présentent le gros désavantage de ne permettre de doser que la forme active du tryptophane (L-tryptophane) STOCKES, et ses coll.[64]. Or le tryptophane se racémise assez facilement lors de l'hydrolyse des protéines. Cette réaction a été étudiée entre autres par SPIES ET CHAMBERS[62] dans le cas de solutions alcalines (NaOH 5 N pendant 18 h). Dans des solutions acides, GREENHUT et ses coll.[24] ont montrés que le L-tryptophane perd 25% de son activité par chauffage en autoclave (HCl 2 N pendant 2 h) et qu'il se produit déjà une racémisation par chauffage en autoclave avec de l'eau distillée. Leur principal avantage réside dans le fait qu'elles sont spécifiques. Par exemple, l'acide indolylacétique, indolylpropionique et d'autres composés possédant une structure voisine de celle du tryptophane n'interfèrent pas lors du dosage WOOLEY ET SEBRELL[78].

Les méthodes chimiques ont l'avantage sur les méthodes biologiques d'être plus rapides et de donner aux résultats une meilleure reproductibilité. Cependant elles sont souvent moins spécifiques.

L'historique du développement des méthodes chimiques de dosage du tryptophane se trouve exposé dans le livre de BLOCK ET BOLLING[8] où il est fait mention d'un certain nombre de méthodes qui emploient la réaction colorée que donne le groupement indolique du tryptophane avec les oxydants:
$NaOCl$ MILLER ET LYONS[42]. — $NaNO_2$. A. HOMER, (p. 345)[32] ainsi que LUGG[40]. — $FeCl_3$ en présence de HCl. A. O. M. STOPPANI[65]. — HNO_3 et H_2SO_4. ROTH ET SCHUSTER[55]. Cette méthode a été employée par SCHORMULLER[37] pour doser le tryptophane libre et protéinique dans les denrées alimentaires.

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La méthode de ALBANESE ET FRANKSTON[2,3] fait appel au nitrite de sodium, au persulfate de potassium et à une solution de thymol. Celle de YOSHIDA[79] se sert de la coloration que donne le tryptophane avec une solution de brome en présence de méthylorange. Citons encore la méthode OSBORNE et ses coll.[47] où le tryptophane est dosé sous forme d'humine. Cette dernière est obtenue par chauffage à ébullition (24 h) de la solution de tryptophane en présence de glucose. Les auteurs montrent qu'environ le 86% des molécules de tryptophane contribue à la formation d'humine.

Les méthodes les plus importantes sont cependant celles où une coloration est obtenue par oxydation du complexe que forme le tryptophane avec les aldéhydes: VOISENET[73] et RHODE[51]. Un grand nombre d'aldéhydes donne cette réaction: Le *formaldéhyde:* FURTH ET DISCHE[16]. — KOMM[37]. — RAPOPORT ET EICHINGER[49]. — ROSENHEIM[53]. — TILLMANNS ET ALT[69]. — *L'aldéhyde salycilique:* FEARON[14]. — REICHL[50]. — *La vanilline:* KRAUS[38] ET RAGINS[48]. Les aldéhydes actuellement les plus employés sont: le *p-diméthylaminobenzaldéhyde:* (*p*-DAB) THOMAS[68]. — MAY ET ROSE[41]. — FURTH ET DISCHE[16]. — KRAUS[38]. — KOMM[37]. — TOMIYAMA ET SHIGEMATSU[70]. — HORN ET JONES[34]. — SPIES ET CHAMBERS[62]. — et *l'acide glyoxylique:* ADAMKIEWICKS[1]. — HOPKINS ET COLE[33]. — CARY[11]. — FEARON ET WINKLER[76]. — CARPENTIER[10]. — STAUB ET BOSSHARDT[63].

Certains composés ayant une structure voisine de celle du tryptophane comme la tryptamine, l'acide indolylpropionique, l'acide indolylacétique, le tryptophole et le scatole donnent une réaction analogue à celle du tryptophane avec les aldéhydes. La réaction colorimétrique du tryptophane avec les aldéhydes n'est donc pas une réaction tout à fait spécifique.

I. MÉCANISME DE LA RÉACTION

L'identification du composé qui, par oxydation, donne la coloration bleue servant au dosage du tryptophane et l'explication de la réaction des aldéhydes avec les dérivés du tryptophane, n'ont pas encore abouti à une solution tout à fait satisfaisante.

BRUSTLER et ses coll.[9] pensent que le complexe du tryptophane avec les aldéhydes est obtenu grâce à la présence, dans ce dernier, d'une chaîne latérale. Ils remarquent que la réaction est positive pour le scatole, l'α-méthylindole, le tryptophane, la tyrothricine, la gramicidine, alors qu'elle est négative pour l'indole, le carbazole, la brucine.

Ces exemples montrent que la condition nécessaire pour qu'un dérivé de l'indole donne la coloration bleue est de posséder une chaîne latérale; il serait cependant imprudent de déduire de ces constatations que la condensation de l'aldéhyde avec le tryptophane se fait exclusivement avec cette chaîne latérale. En effet, l'α-oxytryptophane isolé par WIELAND ET WITKOP[75] ne donne pas la réaction de HOPKINS ET COLE[33]. La présence d'une chaîne latérale ne suffit donc

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pas, il faut comme seconde condition que la position *α* (position 2) du cycle indolique soit libre.

D'après GIRAL ET LAGUNA[18], les deux conditions énumérées ci-dessus ne suffisent pas. Il faut, comme troisième condition, que la position 1 du cycle indolique soit libre. La présence d'un substituant (méthyle) sur l'azote du cycle indolique empêche la formation de la coloration bleue, alors que la monométhylation de l'azote de la chaîne latérale du tryptophane n'a aucune influence sur la formation de cette coloration et que l'hypaphorine, où l'azote de la chaîne latérale est complètement substitué, donne aussi la coloration. La réactivité des aldéhydes avec l'azote indolique est confirmée par VELUZ[72] pour le tryptophane protéinique contenu dans la toxine du tétanos et par ROSS ET STANLEY[54] pour le virus de la mosaïque du tabac.

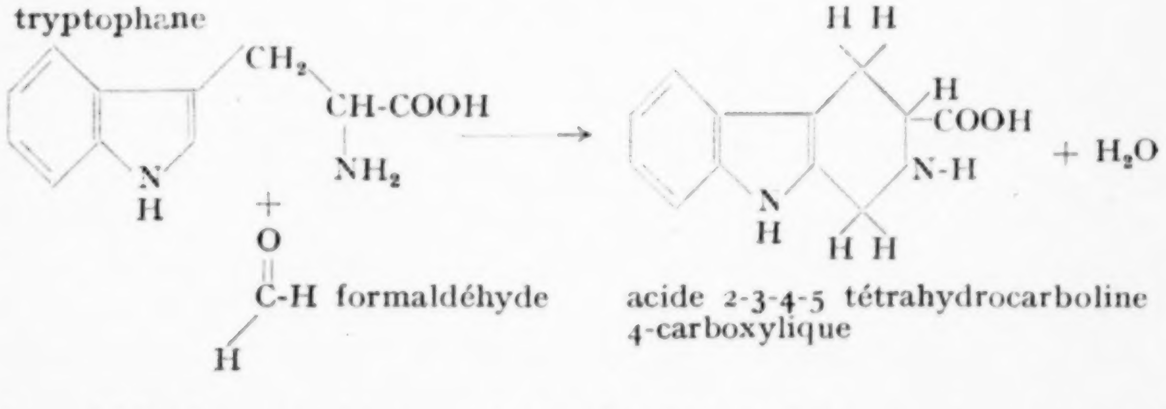
D'une façon générale, l'aldéhyde ne substitue pas le cycle indolique en position 1, mais en position 2. On peut se demander pourquoi l'azote du cycle (position 1) doit être libre pour que la réaction ait lieu.

D'après FRAENKEL-CONRAT et ses coll.[15], l'aldéhyde réagit en premier avec l'azote de l'indole, il se produit ultérieurement une migration du substituant de la position 1 en position 2. Ceci est d'autant plus probable que le transfert d'électrons se fait avec une grande facilité sur le cycle indolique, BAKER et ses coll.[5].

Tous les auteurs sont généralement d'accord d'admettre que la formation de la coloration se fait en deux temps:

1. Condensation du dérivé indolique avec l'aldéhyde.
2. Oxydation du produit de condensation.

Avant de pouvoir préciser la nature du composé qui donne la coloration, il faut tout d'abord connaître celle du complexe „aldéhyde-tryptophane". HOLDEN ET FREEMAN[29] pensent que la formation d'un composé stable du formaldéhyde avec le tryptophane est due à la création d'un nouveau cycle d'après le schéma:



Le formaldéhyde se combine aussi avec les dérivés du tryptophane comme le scatole, l'acide indolacétique, le 2-3 et le 1-3-diméthylindole en solution acide, mais cependant dans ce cas la formation d'un cycle est improbable et la formation du complexe ne correspond pas au schéma indiqué ci-dessus.

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La réactivité n'est pas toujours la même suivant l'aldéhyde considéré. Ainsi d'après HAHN et ses coll.[25], le benzaldéhyde se condense avec la tryptamine avec un rendement de 48% alors que la condensation avec le glyoxal et la vanilline ne peut pas être obtenue. La préparation d'une série de dérivés β-carboline (à partir de tryptophane) est décrite dans le travail de SNYDER et ses coll.[61].

Parmi les autres acides aminés, l'histidine se combine aussi avec les aldéhydes en formant un cycle analogue au tryptophane. Cependant l'oxydation de ce complexe n'aboutit pas à la formation d'une coloration.

Le problème dans son ensemble est très complexe. Cependant les travaux de HARVEY et ses coll.[26] montrent d'une façon précise que par oxydation de l'acide tétrahydrocarbolinecarboxylique l'on obtient la coloration bleue caractéristique. Ils prouvent ainsi, pour quelques uns des dérivés du tryptophane, que la formation d'un cycle (dérivé β-carboline) par condensation de ces dérivés avec les aldéhydes, représente bien le terme intermédiaire de la réaction et que l'oxydation du complexe produit la coloration.

Les exemples donnés par HARVEY et ses coll.[26] ne concernent que les complexes du tryptophane et du N-méthyl-tryptophane avec le formaldéhyde, l'acétaldéhyde et le benzaldéhyde.

La nature de la coloration obtenue avec le scatole ne peut être expliquée par la formation d'un cycle carboline. La formation d'un tel cycle pourrait éventuellement être obtenue, s'il se produisait au préalable une rupture de la liaison 2-3 du cycle indolique.

MULLER[44] a étudié, pour des composés possédant une structure voisine du tryptophane, la coloration des produits de condensation avec le *p*-DAB* en présence d'acide acétique et d'acide phosphorique. La coloration qu'il obtient, n'est cependant pas identique à la coloration bleue obtenue en solution d'acide chlorhydrique ou sulfurique.

2. DOSAGE DU TRYPTOPHANE DANS LES PROTÉINES

L'hydrolyse de la protéine, qu'elle soit faite en solution acide ou alcaline produit généralement une destruction partielle du tryptophane. Cette destruction est catalysée par la présence d'ions Cu^{+2} et Co^{+2} qui ont déjà une activité pour des concentrations de $5 \cdot 10^{-6}$ Mol. g par litre, DAWES ET HAPPOLD[13]. Les données de la littérature qui concernent la destruction du tryptophane lors de l'hydrolyse des protéines sont souvent contradictoires. En milieu alcalin, la stabilité du tryptophane a été étudiée par KUIKEN et ses coll.[39]. La destruction du tryptophane est déterminée par la mesure de la quantité d'oxygène absorbée. Une étude, faite pour différentes concentrations de la solution en soude caustique, montre que le maximum de destruction est obtenu pour des solutions 4 *N*. Il est peut-être intéressant de noter qu'à la concentration de la solution de soude caustique où la destruction du tryptophane est maximum, correspond aussi la conductibilité électrique maximum.

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* *p*-DAB: *p*-diméthylaminobenzaldéhyde

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En solution acide le tryptophane pur est plus ou moins stable suivant la concentration en acide. La stabilité semble complète en solution d'acide sulfurique 0.5 *N* (chauffage sous pression pendant 5 h) SAHYUN[56]. Cet auteur montre d'autre part que, dans les mêmes conditions, d'autres acides aminés tels que la thréonine, la sérine, la cystine et la cystéine ou simplement les acides aminés contenus dans un hydrolysat de protéines, produisent une destruction appréciable du tryptophane. Il s'agit d'un phénomène d'oxydo-réduction: à l'oxydation du tryptophane correspond la réduction de la cystine en cystéine (OLCOTT ET FRAENKEL-CONRAT[46]).

Dans des solutions d'acide sulfurique concentré, la destruction du tryptophane pur se produit déjà à la température ambiante. GIRAL[17] ne retrouve que le 67% du tryptophane introduit dans une solution d'acide sulfurique concentré après une durée de 1 jour.

Nous avons étudié la stabilité du tryptophane pur et du tryptophane contenu dans la caséine pour des solutions d'acide sulfurique 19 *N* (62%). Les résultats sont résumés dans le tableau 1.

TABLEAU I

STABILITÉ DU TRYPTOPHANE PUR ET DU TRYPTOPHANE CONTENU DANS LA CASÉINE DANS DES SOLUTIONS D'ACIDE SULFURIQUE 19 *N* POUR UNE DURÉE DE 1 JOUR

	Tryptophane introduit	Tryptophane retrouvé	Pertes en %
Tryptophane pur	0.102	0.85	17
	0.153	1.27	17
Tryptophane contenu dans la caséine (10.0 mg dans 10 ml, - 1.17% de trypt.)	0.117	0.067	37

La plupart des méthodes modernes de dosage du tryptophane ne nécessitent plus une hydrolyse de la protéine avant le dosage. Par exemple, BATES[6] se contente de disperser le caséine dans une solution de soude caustique *N*/10, à la température ambiante, pendant 5-10 minutes. Pour d'autres protéines, la dispersion dans des solutions de soude caustique ne donne pas des résultats aussi favorables et après quelques essais de dispersion des protéines dans le borax par exemple, il semble bien qu'il ne soit pas possible de trouver une méthode de dispersion qui s'applique à n'importe quelle protéine. La méthode de CLARK (1951) où la dispersion de la protéine est facilitée par traitement de la substance dans de l'urée fondue (P.F. 132°) donne de bons résultats quant à la dispersion, mais l'influence du chauffage produit dans le cas de la caséine une destruction d'environ 30% de tryptophane.

Spies et Chambers[62] ont renoncé à un traitement préalable de la protéine avant l'analyse. La haute concentration en acide (SO_4H_2 environ 62%) du milieu où se forme le complexe du tryptophane avec l'aldéhyde produit une hydrolyse suffisante de la protéine pour permettre au tryptophane d'être dosé colorimétriquement. Cependant, après un séjour d'un jour dans une solution d'acide fort, à la température ambiante, il ne se produit qu'une légère hydrolyse de la protéine. Arber[4] a mesuré la variation du poids moléculaire moyen des peptides obtenus après un séjour dans une solution d'acide sulfurique à 50%, à la température ambiante. Le poids moléculaire moyen obtenu après un jour d'hydrolyse est environ dix fois supérieur à celui obtenu après hydrolyse pendant une année.

Par ailleurs, l'adjonction de *p*-diméthylaminobenzaldéhyde (*p*-DAB) à la solution d'acide sulfurique contenant le tryptophane, produit une stabilisation de ce dernier en agissant probablement comme antioxydant.

3. TENEUR EN TRYPTOPHANE DE LA CASÉINE

On obtient, lors de la comparaison des résultats de dosage du tryptophane dans les protéines, deux séries de résultats qui dépendent des méthodes employées. Les méthodes au *p*-DAB en présence d'acide chlorhydrique telles qu'elles ont été décrites par May et Rose[41] (coloration obtenue sans l'action d'oxydant), par Holm et Greenbank[31] (sans oxydant, durée de réaction plus longue que pour la méthode de May et Rose), par Sullivan et ses coll.[67] (chauffage de la protéine 15 minutes à 85°, oxydation du complexe par H_2O_2), par Shaw et McFarlane[60] (chauffage 1 jour à 37°, ensuite oxydation par H_2O_2), donnent pour le dosage du tryptophane dans la caséine des valeurs de l'ordre de 2.2 à 2.5% par rapport à la substance séchée à l'air. Ces valeurs représentent environ le double de celles obtenues par la méthode à l'acide glyoxylique qui sont d'environ 1.1 à 1.4% Staub et Bosshardt[63], Shaw et McFarlane[60] et Carpentier[10].

Il semble que les valeurs obtenues par la méthode à l'acide glyoxylique soient plus près de la réalité que celles fournies par les méthodes au *p*-DAB citées ci-dessus. En effet, les déterminations microbiologiques de Rockland et Dunn[52] donnent des valeurs de 1.15 — 1.36%. Cet ordre de grandeur est confirmé par les mesures de Holiday[30] où la teneur en tryptophane est mesurée par spectrophotométrie dans l'ultra-violet et par une méthode où Shaw et McFarlane[60] ont isolé et pesé le tryptophane contenu dans un hydrolysat de caséine.

Block et Bolling[8] pensent que les méthodes qui emploient le *p*-DAB en solution d'acide chlorhydrique donnent des résultats trop élevés parcé qu'elles ne sont pas suffisamment spécifiques. Cette conclusion laisse supposer qu'une

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partie de l'intensité de la coloration obtenue provient de composés dérivant du tryptophane ou ayant une structure voisine.

Pour vérifier ces hypothèses nous avons étudié les colorations obtenues d'une part par les méthodes au *p*-DAB et d'autre part par celles à l'acide glyoxylique avec les produits les plus simples de la dégradation du tryptophane: la tryptamine, l'acide indolylpropionique, l'acide indolylacétique, et l'indole. Tous ces composés donnent pour chacune des deux méthodes une teinte semblable, et pour des concentrations moléculaires équivalentes des intensités de coloration à peu près égales. Seul l'indole ne produit pas la coloration caractéristique des autres composés. Les conclusions de BLOCK ET BOLLING[8] sont donc fausses.

Pour SHAW ET MCFARLANE[60], les résultats erronés obtenus lors du dosage des protéines par les méthodes au *p*-DAB citées ci-dessus proviennent du fait que le tryptophane contenu dans les protéines (tryptophane lié) donne une coloration plus intense que le tryptophane libre. Ils pensent que le mode de liaison et le degré d'oxydation jouent un rôle dans la coloration. LUGG[40] n'est cependant pas parvenu à démontrer que l'accroissement de la coloration soit dû à des liaisons peptidiques.

Nous pensons que cette discordance entre les différents résultats d'analyse du tryptophane ne dépend, ni de la spécificité de la méthode, ni du mode de liaison du tryptophane. Nous discuterons ultérieurement les causes de ces différences après avoir donné quelques résultats d'analyse du tryptophane dans la caséine, en employant 3 méthodes différentes au *p*-DAB: 1) de SPIES ET CHAMBERS[62] (méthode B) — 2) de BATES[6] — 3) de SHAW ET MCFARLANE[60]. Les résultats sont donnés dans le tableau II.

TABLEAU II

ANALYSE DU TRYPTOPHANE DANS LA CASÉINE PURUM SIEGFRIED PAR TROIS MÉTHODES DIFFÉRENTES AU *p*-DAB

Méthode	Poids de la caséine dans un essai	Teneur en tryptophane de la caséine séchée à l'air
SPIES ET CHAMBERS *p*-DAB avec H_2SO_4	7.70 mg/10 ml	1.17%
	7.9	1.16
	10.0	1.17
	12.5	1.18
	13.5	1.18
BATES *p*-DAB avec HCl	10.7 mg/50 ml	1.50%
	26.8	1.20
	37.6	1.17
		Calculé par la méthode de DANNACHER 1.14%
SHAW ET MCFARLANE	26.8 mg/50 ml	2.48%
	62.0	2.47

TABLEAU III

VARIATION DE L'ABSORPTION DES SOLUTIONS (619 mμ) CONTENANT DE LA CASÉINE ET DU TRYPTOPHANE PUR, EN FONCTION DU TEMPS (SPECTROPHOTOMÈTRE PULFRICH) (CUVE DE 1 cm)

Durée de chauffage de la solution à 37°	Coefficient d'absorption (50.0 ml de solution)						
	caséine			tryptophane			
	25.2 mg	50.0	béta[2]	0.515 mg	0.258	alpha[1]	%
Sans oxydant				A			
4 h	colorée	colorée	—	incolore	incolore	—	infini
23 h	0.218	0.342	0.500	0.0514	0.0290	0.087	5.9%
4 j	0.331	0.608	1.12	0.191	0.092	0.385	2.9
6 j	0.331	0.595	1.17	0.219	0.102	0.455	2.6
8 j	0.314	0.570	1.03	0.255	0.123	0.514	2.0
13 j	0.254	0.475	0.89	0.278	0.119	0.619	1.4
18 j	0.212	0.409	0.79	0.265	0.111	0.600	1.3
Avec oxydant 0.25 ml H_2O_2 30% dans 50 ml				B			
(a) 4 h	0.354	0.692	1.36	0.455	0.200	0.99	1.37%
23 h	0.430	0.797	1.48	0.559	0.233	1.27	1.17
4 j	0.398	0.770	1.50	0.541	0.193	1.35	1.11
6 j	0.370	0.716	1.40	0.512	0.190	1.26	1.11
8 j	0.350	0.672	1.30	0.499	0.183	1.23	1.06

[1] alpha est le coefficient angulaire de la droite d'étalonnage

$$\text{alpha} = \frac{0.455-0.200}{0.515-0.258} \cdot 1.00 = 0.99$$ (calcul effectué pour le cas (a));

[2] béta est le coefficient angulaire de la droite qui exprime l'extinction en fonction de la teneur en caséine.

$$\text{béta} = \frac{0.692-0.354}{50.0 - 25.2} \cdot 100 = 1.36$$ (calcul effectué pour le cas (a))

En divisant béta/alpha on obtient la teneur en tryptophane de la caséine par la méthode de DANNACHER[12].

Dans le Tableau II, la méthode de BATES donne des teneurs de tryptophane qui varient avec le poids de l'échantillon dosé. Ceci est dû au fait que la droite d'étalonnage ne passe pas par l'origine du système d'axes ,,extinction — poids de tryptophane". Pour cette méthode, la teneur réelle en tryptophane calculée par la méthode de DANNACHER[12] est de 1.14%.

Il en résulte que la concordance entre les résultats obtenus par la méthode de SPIES ET CHAMBERS et par celle de BATES est bonne. La méthode de SHAW ET MCFARLANE donne des résultats trop élevés. Nous essayerons par la suite de démontrer pour quelles raisons la méthode de SHAW ET MCFARLANE donne des résultats erronés, mais auparavant il faut remarquer que la teneur en tryptophane obtenue au moyen de la méthode de BATES correspond avec la teneur généralement admise. Ainsi, contrairement aux indications données par BLOCK ET BOLLING[8], la méthode au *p*-DAB en présence d'acide chlorhydrique telle qu'elle est prescrite par BATES n'est pas moins spécifique que la méthode à l'acide glyoxylique.

4. ÉTUDE DE LA FORMATION DE LA COLORATION DU TRYPTOPHANE AVEC LE *p*-DAB EN PRÉSENCE D'ACIDE CHLORHYDRIQUE

Le procédé le plus simple pour étudier cette réaction consiste à placer des échantillons de caséine et de tryptophane pur dans des solutions d'acide chlorhydrique à 20% en présence de *p*-DAB (100 ml de la solution finale contiennent 1 ml d'une solution à 5% de *p*-DAB dans H_2SO_4 à 10%). Le mélange est placé à l'étuve à 37°. On prélève de temps en temps un certain volume de solution dont on mesure l'extinction (Tableau III A). A un autre prélèvement, on ajoute un oxydant (H_2O_2), la coloration s'intensifie aussitôt puis décroît. On mesure dans ce second cas le maximum de l'absorption. Les résultats de ces mesures sont donnés dans le Tableau III B.

A. *Formation de la coloration sans action de l'eau oxygénée* (*Tableau III A*)

Dans ce cas l'oxydation du complexe „aldéhyde — tryptophane" se fait lentement par l'action de l'oxygène de l'air. Le développement de la coloration est plus rapide dans le cas de la caséine que dans celui du tryptophane pur. Le maximum de l'intensité de la coloration en fonction du temps est plus rapidement obtenu pour la caséine que pour le tryptophane pur. Il n'est donc pas exact de comparer les intensités de coloration de la solution contenant la caséine et de celle qui contient le tryptophane pour une même durée de réaction avec le *p*-DAB. En comparant les valeurs maxima d'alpha (après 13 jours) et de béta (après 6 jours) du tableau III A, on obtient une teneur en tryptophane de 1.9%. Cette valeur est trop élevée, ceci doit provenir du fait qu'entre le sixième et le treizième jour une partie du tryptophane pur de la solution a déjà dû être détruite, d'où il résulte une diminution de l'intensité de la coloration de l'étalon.

B. *Augmentation de la vitesse de développement de la coloration par oxydation au moyen d'eau oxygénée* (*Tableau III B*)

Dans ce second cas, l'intensité de la coloration est nettement supérieure à celle obtenue sans l'action de l'eau oxygénée. Comparativement, la coloration du tryptophane pur est beaucoup plus forte. Il en résulte que la teneur en tryptophane de la caséine qui est de 1.17% pour le maximum d'intensité des colorations, correspond bien à la valeur généralement admise.

C. *Discussion des résultats*

Les essais résumés dans le tableau III montrent le rôle important que joue l'oxydant dant la réaction colorimétrique. Si la quantité d'oxydant n'est pas suffisamment grande le développement de la coloration de la solution contenant le tryptophane pur est moins accentué que dans le cas de la caséine. Il en résulte que la teneur en trytophane de la protéine paraît trop élevée.

Comme nous l'avons vu précédemment la méthode de Shaw et McFarlane[60] donne des teneurs en tryptophane environ double de celle que semble réellement contenir la caséine. Si l'on ne change, de cette méthode, que la durée de chauffage à 37° et que l'on étende cette durée de 1 jour à 18 jours, la teneur en tryptophane de la caséine passe de 2.5% à 1.2%. La Figure 1 montre particulièrement bien l'accroissement de l'intensité de la coloration de la solution contenant le tryptophane pur entre 1 et 18 jours alors que l'on note une légère diminution pour les solutions de caséine.

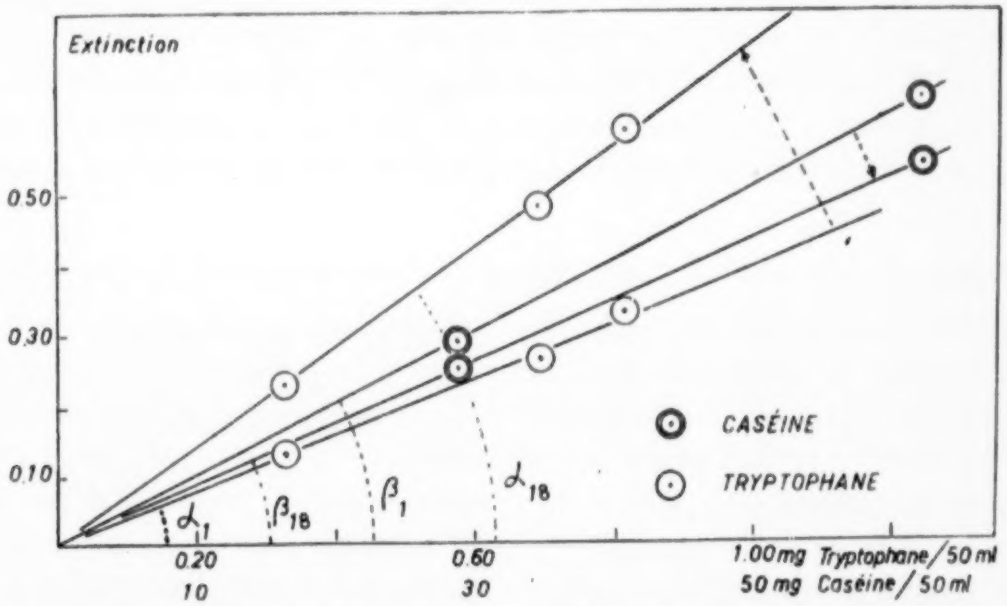

Fig. 1. Dosage du tryptophane par la méthode de Shaw et McFarlane[59] en employant le p-DAB en présence d'HCl.

Il est important de noter que, contrairement aux affirmations de Block et Bolling[8], les résultats erronés obtenus par les méthodes au p-DAB en présence d'HCl ne proviennent pas du manque de spécificité de ces méthodes mais, comme l'avaient déjà suggéré Sullivan et Hess[66], d'une différence dans le degré de développement de la coloration, d'une part dans des solutions de tryptophane pur, d'autre part dans celles contenant des protéines. C'est pour cette raison qu'il n'est pas exact d'établir une correspondance entre le rapport de l'absorption de ces solutions et la concentration en tryptophane. C'est pour cette même raison que les méthodes de May et Rose[41] et Shaw et McFarlane[60] donnent des résultats erronnés. Les teneurs trop élevées obtenues par ces auteurs s'expliquent aisément en considérant la Fig. 1. Le degré de développement (après 1 jour) de la coloration de la solution contenant le tryptophane pur est plus petit que celui de la solution contenant la protéine. La teneur en tryptophane de la protéine paraît donc plus grande.

Remarquons cependant que l'adjonction d'une certaine quantité d'oxydant augmente fortement les vitesses de développement de la coloration dans les deux cas. Elles deviennent alors sensiblement égales. Il en résulte que pour une même durée de réaction, le degré de développement de la coloration devient à peu près équivalent si l'on considère une solution de tryptophane pur ou une solution contenant une protéine. Il est donc possible d'employer, dans ce cas, la courbe d'étalonnage (tryptophane pur) pour calculer la teneur en tryptophane d'une protéine. Ces affirmations sont confirmées par les résultats obtenus par la méthode de BATES[6] (*p*-DAB, en présence d'HCl et d'un oxydant) qui correspondent à ceux généralement admis (Tableau II).

5. COMPARAISON DE QUELQUES MÉTHODES DE DOSAGE DU TRYPTOPHANE

Parmi les méthodes chimiques de dosage du tryptophane dans les protéines, il est relativement assez difficile de faire un choix, chaque méthode présentant certains avantages et certains inconvénients.

Comme nous l'avons montré, les méthodes au *p*-diméthylaminobenzaldéhyde (*p*-DAB) en présence d'acide chlorhydrique peuvent donner d'aussi bons résultats que les autres méthodes. Par exemple, la méthode de BATES[6] a l'avantage d'être rapide. Sa précision, d'après l'auteur, est de l'ordre de 2-3%. Son principal désavantage réside dans le fait que la droite d'étalonnage ne passe pas par l'origine du système d'axes „extinction — poids de tryptophane" et qu'il faille employer la méthode de DANNACHER[12] pour calculer la teneur en tryptophane de la protéine.

La méthode de SPIES ET CHAMBERS[62] (modification B, 1948) a le grand avantage d'avoir été étudiée dans le détail. En outre, pour des solutions contenant des protéines, la mesure de l'extinction est directement proportionnelle à la concentration en tryptophane. Son principal désavantage réside dans le fait que la

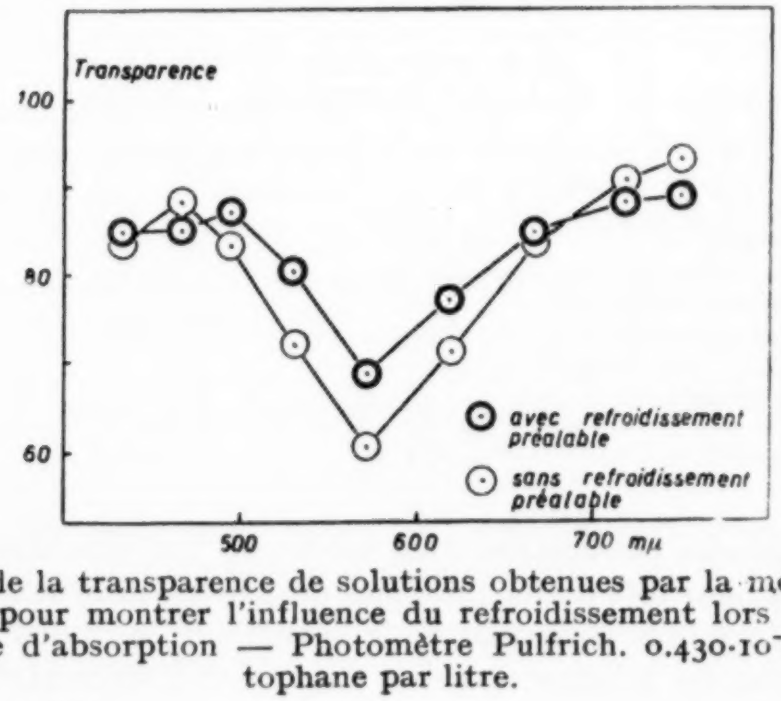

Fig. 2. Mesure de la transparence de solutions obtenues par la méthode de STAUB ET BOSSHARDT pour montrer l'influence du refroidissement lors du mélange des réactifs. Spectre d'absorption — Photomètre Pulfrich. $0.430 \cdot 10^{-4}$ mole de tryptophane par litre.

quantité d'oxydant employée pour développer le maximum de coloration est différente suivant la protéine considérée.

La méthode à l'acide glyoxylique, telle qu'elle a été décrite par STAUB ET BOSSHARDT[63], a le désavantage dep résenter deux sortes de coloration suivant la manière de mélanger les réactifs. L'échauffement produit par la dilution de la solution d'acide sulfurique concentré a une nette influence sur la coloration obtenue. La figure 2 montre les spectres d'absorption que l'on obtient soit en refroidissant la solution 1 à 2 minutes après le mélange, soit en refroidissant les réactifs avant et pendant le mélange.

Pour obtenir des valeurs reproductibles dans leurs essais, STAUB ET BOSSHARDT[63] font les lectures de l'absorption à 650 mμ, longueur d'onde pour laquelle l'absorption est à peu près équivalente, quelle que soit la manière dont a été effectué le mélange. Cette longueur d'onde ne correspond pas au maximum d'absorption et de ce fait cette méthode à l'acide glyoxylique est environ 4 à 6 fois moins sensible que les autres méthodes. Comme pour la méthode de BATES, la teneur en tryptophane des protéines doit être calculée par la méthode de DANNACHER.

Nous avons résumé dans le tableau IV quelques-unes des caractéristiques des différents types de méthodes de dosage du tryptophane. Les résultats d'analyse par la méthode à l'acide glyoxylique sont tirés du travail de STAUB ET BOSSHARDT (hydrolyse préalable de la caséine avec de la soude caustique). Les autres résultats sont obtenus en plaçant les échantillons de caséine (température ambiante-NaOH N/10) après une dispersion dans de la soude caustique, directement dans les solutions de réactifs.

TABLEAU IV

QUELQUES CARACTÉRISTIQUES DE TROIS TYPES DIFFÉRENTS DE MÉTHODES DE DOSAGE DU TRYPTOPHANE

	Acide glyoxylique STAUB ET BOSSHARDT	p-DAB HCl BATES	p-DAB H_2SO_4 SPIES ET CHAMBERS
Teneur en tryptophane de la caséine (par rapport à la substance séchée à l'air)	1.12%	1.14%	1.17%
Sensibilité (coefficient angulaire de la droite d'étalonnage — extinction par mg de tryp. dans 50 ml de solution)	0.25	1.58	1.11
Durée de l'opération	1/2 h	1/2 h	3/2 h

Dans une prochaine publication nous donnerons une série d'analyses de tryptophane contenu dans différentes protéines et denrées alimentaires. Nous avons, d'une part, employé la modification B de la méthode de SPIES ET CHAMBERS[62]. D'autre part, pour les substances qui se dispersent lentement dans l'acide sulfurique 19 N, nous avons prolongé la durée de développement de la coloration de 30 minutes à 24 heures. Des essais de contrôle nous ont permis d'établir qu'il n'y avait pas de modification de l'intensité de la coloration, pour des solutions de tryptophane pur, lorsque la durée de développement était augmentée à un jour. L'emploi de l'acide sulfurique a été préféré à celui de l'acide chlorhydrique parce que la destruction du tryptophane est moins importante en solution sulfurique (OLCOTT ET FRAENKEL-CONRAT[45]) et que la dispersion des substances protéiniques contenant le tryptophane à doser se produit toujours dans l'acide sulfurique 19 N employé pour la réaction colorimétrique.

Le seul inconvénient de la méthode réside dans le fait que la dispersion nécessite généralement 1 jour pour être complète et qu'il n'est pas impossible qu'il se produise déjà une légère décomposition du trytophane. La présence de p-DAB dans la solution doit empêcher en grande partie cette destruction.

PARTIE EXPÉRIMENTALE

1. *Méthode à l'acide glyoxylique de* STAUB ET BOSSHARDT[63]

Réactifs

1. *Solution d'acide glyoxylique.* On introduit 10 g de magnésium en poudre dans un erlenmeyer. On recouvre d'une couche d'eau (20 ml) et on refroidit. On introduit ensuite par petites portions 250 ml d'une solution à 10% (P/V) d'acide glyoxylique. Après une demi-heure on filtre et on ajoute un ml d'acide acétique. La solution est ainsi prête pour le dosage.
2. *Alcool industriel*
3. *Acide sulfurique concentré*

Méthode

Dans un cylindre gradué de 25 ml à bouchon émeri on introduit 1.00 ml d'une solution de tryptophane (0.5 mg) puis 0.50 ml d'alcool industriel. On laisse ensuite couler lentement le long des parois 8.00 ml d'acide sulfurique concentré. On refroidit la solution sous le robinet. On mélange ensuite les solutions en continuant de refroidir. On mesure l'extinction après 20 minutes au photomètre (Lumetron 400 A 650 mμ) (Pulfrich 666 mμ).

2. *Méthode à l'acide glyoxylique de* CARPENTIER[10].

Réactifs

1. *Solution d'acide glyoxylique.* 0.004 M. On dilue 5.00 ml de la solution obtenue par STAUB ET BOSSHARDT à 1.00 litre.
2. *Sulfate de cuivre* 0.01 M
3. *Acide sulfurique concentré*

Bibliographie p. 44/45.

Méthode

On introduit dans un flacon de 10.0 ml, 0.2 à 1.5 ml d'une solution 0.0005 M de tryptophane puis 0.2 ml d'une solution d'acide glyoxylique 0.004 M et 0.3 ml d'une solution de sulfate de cuivre 0.01 M. La solution est refroidie dans un bain de glace. On ajoute goutte à goutte 5.00 ml d'acide sulfurique conc. en agitant et en refroidissant. On laisse reposer 20-30 minutes à la température de la chambre. On place ensuite l'échantillon 20 minutes au bain-marie. Lecture au photomètre Beckman en quartz 2800, 3700 et 5700 mμ.

3. *Méthode au* p-*DAB en présence de HCl de* SHAW ET MCFARLANE[60].

(*Procédé modifié*)

Réactifs

1. *Solution d'acide chlorhydrique à* 21%. (1 volume de HCl 39% + un volume d'eau distillée)
2. *Solution de* p-*DAB* à 5% dans H_2SO_4 à 10%
3. *Solution d'eau oxygénée* à 3%

Méthode

Un échantillon de protéine contenant environ 0.5 mg de tryptophane est placé dans un flacon jaugé de 20 ml. On ajoute 0.2 ml d'une solution à 5% de *p*-DAB et on remplit jusqu'au trait avec la solution d'acide chlorhydrique à 21%. On place le récipient 24 h à 37°. On prélève ensuite 5 ml que l'on verse dans 15 ml d'eau distillée. On ajoute 0.15 ml d'une solution d'eau oxygénée à 3%. Le maximum de coloration est obtenu après 30-40 minutes; il dure 10-15 minutes.

4. *Méthode au* p-*DAB en présence d'HCl de* BATES[6]

Réactifs

1. *Solution d'acide chlorhydrique* 39%
2. *Solution de* p-*DAB* à 5% dans H_2SO_4 à 10%
3. *Solution de nitrate de sodium* à 1%

Méthode

On pèse dans un bécher de 25 ml une quantité de protéine contenant environ 0.5 mg de tryptophane. On ajoute 2 ml d'une solution de NaOH $N/10$. On agite avec une baguette de verre jusqu'à dispersion complète de la protéine. On ajoute alors 0.50 ml d'une solution à 5% de *p*-DAB, et 0.2 ml d'une solution de NO_3Na à 1%.

On prépare dans un cylindre gradué 25 ml de HCl 39%. On verse 10 ml dans le bécher et on fait ensuite passer la solution dans un ballon jaugé de 50 ml. On rince le bécher avec le reste de la solution d'acide chlorhydrique conc. que l'on verse aussi dans le ballon jaugé. On laisse reposer exactement 15 minutes. On remplit ensuite le ballon jaugé avec de l'eau distillée. On obtient généralement le maximum de coloration après 15 minutes.

5. *Méthode au* p-*DAB en présence de H_2SO_4 de* SPIES ET CHAMBERS[62]

Réactifs

1. *Solution d'acide sulfurique* 23.8 *N*. Un litre de solution contient 665 ml SO_4H_2 96% (ps. 1.84).
2. *Solution de* p-*DAB* à 3% dans H_2SO_4 à 10%.
3. *Solution de nitrite de sodium* à 1%. Avant l'emploi on dilue cette solution dans le rapport de 1/25.

Méthode

On introduit dans un cylindre à bouchon émeri de 20 ml une quantité de protéine contenant environ 0.1 mg de tryptophane. On ajoute 1.00 ml d'eau. On agite pour maintenir la substance en suspension. On ajoute ensuite 8.00 ml d'acide sulfurique 23.8 *N*. On agite la solution et on refroidit. On introduit encore 1.00 ml de la solution de *p*-DAB. On agite de nouveau. On place pendant une heure dans un thermostat à 25°.

On ajoute ensuite 0.1 ml d'une solution de NO_2Na à 0.04%. On agite la solution, la coloration bleue apparaît. On place à nouveau l'échantillon à 25° pendant 1/2 heure. La coloration obtenue est stable. Lecture au photomètre Pulfrich filtre S 61 (619 mμ).

RÉSUMÉ

1. Une grande partie de la littérature se rapportant au dosage chimique du tryptophane et à l'explication de la coloration que donne le tryptophane avec les aldéhydes est passée en revue.

2. Les causes des résultats erronés que l'on obtient en employant la méthode au *p*-diméthylaminobenzaldéhyde, en présence d'acide chlorhydrique, ont été déterminées. Ces résultats erronés ne sont pas dus, comme le pensent certains auteurs, au manque de spécificité de la méthode.

3. Les résultats et la sensibilité de différentes méthodes sont discutés. La méthode qui semble actuellement présenter le plus d'avantages lors du dosage du tryptophane dans les protéines est celle décrite par SPIES ET CHAMBERS [62].

SUMMARY

1. A large part of the literature concerning the chemical determination of tryptophan and the explanation of the coloration given by tryptophan with aldehydes is reviewed.

2. The causes of the erroneous results obtained by using the *p*-dimethylaminobenzaldehyde method, in the presence of hydrochloric acid, have been ascertained.

Contrarily to what some authors think, these erroneous results are not due to a lack of specificity of the method.

3. The results and the sensitivity of various methods are discussed. The most advantageous method for the determination of tryptophan in proteins seems to be — at the present time — the method described by SPIES AND CHAMBERS[62].

ZUSAMMENFASSUNG

1. Ein beträchtlicher Teil der Literatur, welche sich auf die chemische Bestimmung von Tryptophan und auf dessen Farbreaktion mit Aldehyden bezieht, wird besprochen.

2. Bei Anwendung von *p*-Dimethylaminobenzaldehyd in salzsaurer Lösung erhält man fehlerhafte Resultate; die Fehlerquellen dieser Methode wurden ermittelt und gefunden, dass die Fehler nicht, wie gewisse Autoren denken, auf die mangelhafte Spezifität der Methode zurückzuführen sind.

3. Die Ergebnisse und die Empfindlichkeit der verschiedenen Methoden werden erörtert. Die beste Methode für die Bestimmung von Tryptophan in Proteinen scheint heute diejenige von SPIES UND CHAMBERS[62] zu sein.

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SPECTROPHOTOMETRIC STUDIES OF 4- AND 4,7-DIALKYLAMINO-ALKYLAMINO-1,10-PHENANTHROLINES AS THEIR FERROUS CHELATE COMPLEX IONS

by

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INTRODUCTION

The organic complexing agent, 1,10-phenanthroline, has been extensively applied to the solution of numerous problems in quantitative analysis.

A large number of modified 1,10-phenanthroline derivatives have been synthesized in recent years [1-7], and their properties studied as the Fe(II) complex[3] and as the Cu(I) complex[7].

The most important reactions associated with the 1,10-phenanthroline reagents are the following:

1. The formation of complex cations with ferrous ions (the ferroin reaction). Tris-1,10-phenanthroline ferrous complex cations are generally formed although bis- and mono-1,10-phenanthroline ferrous complex cations are also known[8].

2. The formation of complex cations with cuprous ions (the cuproine reaction). Mono- and bis-1,10-phenanthroline chelated cuprous cations are known to exist[7].

Substituted 1,10-phenanthrolines have been studied in which one or more of the possible substitutions for the 2 to 9 hydrogens have been made. The usual ferroin reaction does not apply in case the 2,9-positioned hydrogens are replaced by methyl groups (and probably other groups). Both the ferroin and the cuproine reactions are applicable for all other alkyl substituted 1,10-phenanthrolines. The alkyl groups CH_3, C_2H_5, C_3H_7, and C_6H_5 have been employed in place of one to four of the hydrogens to give symmetrical and unsymmetrical molecules. Nitro, chloro, and bromo acidic groups have likewise been employed. Their ferroin and cuproine complexes are noticeably less stable than their alkyl homologues. The alkyl substituted 1,10-phenanthrolines are extractable using higher alcohols such as *n*-hexyl alcohol as immiscible solvent accompanying either the ferroin or cuproine reaction.

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The analytical applications of the 1,10-phenanthrolines as complexones are as follows:

1. The spectrophotometric determination of iron and of copper.
2. The formation of ferrous complex cations serving as oxidation-reduction indicators.
3. As scavenger complexing agents. This follows the formation of ferrous and cuprous complexes which are extractable by various immiscible solvents providing easily applied separations. Alkyl substituted 1,10-phenanthrolines provide examples of this type scavenger. The removal of traces of iron and of copper from common reagent chemicals may thus be readily accomplished.
4. The application of the ferroin reaction to complex iron to serve as its masking agent[9].
5. The quantitative separation of anions using the Fe(II) phenanthroline complex cations as precipitants. Known procedures have been applied to the separation of ClO_4^- from ClO_3^-, IO_4^- from IO_3^-, $S_2O_8^{-2}$ from SO_4^{-2} and other examples[1].

The present work involves the study of 4- and 4,7-substituted 1,10-phenanthrolines in which long-chain amino groups are employed in the replacement of hydrogen. The ferroin reaction resulting from their use provides a number of departures in effects when compared to those obtained by the alkyl and acidic group substituted complexing agents previously described and so far studied. The present new 1,10-phenanthrolines are applicable as sensitive spectrophotometric reagent for iron and as its scavenger complexing agent. Other simpler members of this series[7] of substituted phenanthrolines are to be preferred and this study is presented with emphasis upon their special properties of possible future analytical significance. These new 1,10-phenanthrolines may be of value in the determination of iron by the use of filter photometers because of their high molecular extinction coefficients as the Fe(II) complex and their broad flat peaks of maximum absorption extending through 50-60 mμ of light source wave lengths.

PREPARATION OF REAGENTS

The modified 1,10-phenanthrolines to be described herein were prepared by SNYDER AND FREIER[10] to be tested for their possible therapeutic value as antimalarial medicinals. Roman numerals will be employed to identify these derivatives to avoid the use of the long scientific names otherwise required.

I. *4,7-bis-(4-diethylamino-1-methylbutylamino)-1,10-phenanthroline.* This preparation results from the coupling of 1-diethylamino-4-aminopentane with 4,7-dichloro-1,10-phenanthroline by heating the reaction mixture at 170 degrees for four hours. The product may be purified by recrystallization from its solution in petroleum ether, (b.p. 85-110) and benzene. Its melting point is 152-155° and molecular weight 492.73. It is sparingly soluble in water and readily soluble as the hydrochloride.

II. *4-(3-diethylaminopropylamino)-1,10-phenanthroline.* This preparation results from the coupling of 3-diethylaminopropylamine with 4-chloro-1,10-phenanthroline by heating the reaction mixture at 160° for 150 minutes. The product may be purified by recrystallization from its solution in methylcyclohexane. Its melting point is 166-168° and molecular weight 308.41.

III. *4,7-bis-(3-diethylaminopropylamino)-1,10-phenanthroline.* This reagent is prepared as described for the corresponding mono-derivative, (II), by substituting 4,7-dichloro-1,10-phenanthroline for the 4-chloro-1,10-phenanthroline. Its melting point is 170-175° and molecular weight 436.63.

EXPERIMENTAL RESULTS

The experimental results employing reagent (III) will be described initially.

The ferroin reaction of compound (III) occurs instantly in water solution producing a very intense red-violet complex. Although addition of dilute acetic acid does not alter this color, the addition of hydrochloric acid causes color conversion to light green. This color reaction is reversed to red-violet upon the addition of ammonia to neutralize the strong acid present.

If the red-violet complex in aqueous solution is allowed to stand at pH 7.0, within 48 hours the red-violet color becomes brown. All attempts to restore the former color after this conversion failed. The red-violet solution has a wave length of maximum absorption at 510 mμ while the green form in solution has lengths of maximum absorption at 581 and 710 mμ.

Identification of the red and green forms of the ferrous complex of phenanthroline (III). Equal molar solutions of ferrous iron and reagent (III) were prepared, ($2.5 \cdot 10^{-3}$ *M*), and mixed in varying proportions. Excess, iron free, hydroxylamine hydrochloride was added for complete reduction of iron. The absorption for each solution was measured first at pH 7 and then at pH 2 by adding the required amount of hydrochloric acid. A period of 2 minutes was allowed for the formation of the green color. The data from these observations is given in Table I and indicates that a tris-complex exists at both pH values.

It should be noted that no color changes were observed for changes of pH in the case of the uncomplexed diamine base. The ferrous complex of reagent (III) is apparently functioning as a pH indicator since the color change is slowly reversed by the addition of acid and base at a pH of approximately 4.5.

Effect of extraction solvents. The ferroin complex of phenanthroline(III) in aqueous acetate and borate buffer at pH 1 to 9 is not extractable by the immiscible solvents *iso*amyl or *n*-hexyl alcohols. However the complex ferrous chelate formed in aqueous solution at pH 7 may be made readily extractable by the addition of ammonium hydroxide.

References p. 56.

Qualitative sensitivity in detection of iron. Phenanthroline(III) as the ferrous complex was tested for sensitivity by mixing small droplets of the reagent solution in a total volume of 0.05 ml. Ammonia fumes were blown over the reaction mixture to adjust the pH for optimum color development. Increased sensitivity was obtained by performing a micro extraction with a droplet of *n*-hexyl alcohol. The following results were obtained:

TABLE I

IDENTIFICATION OF THE RED AND GREEN FORMS OF REAGENT(III) AS THE FERROUS COMPLEX CATION BY APPLICATION OF THE PRINCIPLE OF CONTINUOUS VARIATIONS

Ratio Fe(II)/Reagent(III)	pH 7 Wave Length Max. Absorp. mμ	pH 7 Optical Density	pH 2 Wave Length Max. Absorp. mμ	pH 2 Optical Density
(pure iron)		—		0.020
2:1	509	0.342	578	0.128
1:1	509	0.492	580	0.165
1:2	509	0.702	581	0.229
1:3	510	0.776	580	0.260
1:4	510	0.751	580	0.243
pure reagent (III)		0.018		0.018

Limit of Identification,
  Without extraction — 0.008 γ of Fe
  With *n*-hexyl alcohol extraction — 0.003 γ of Fe
Limit of Concentration
  Without extraction — 1:6,000,000
  With *n*-hexyl alcohol extraction — 1:20,000,000

QUANTITATIVE SPECTROPHOTOMETRIC STUDIES

Spectrophotometric studies to determine the molecular extinction coefficient, wave length of maximum absorption, favorable concentration range for quantitative determination of iron, and other characteristics of the absorption phenomena were carried out. Phenanthroline(III) as the ferrous chelate was investigated both in ammoniacal aqueous solution without extraction and with extraction of the color complex employing *n*-hexyl alcohol. For this work the techniques employed and apparatus used including the Carey recording spectrophotometer, have been described in detail in previous published studies in the same field of reactions[7].

Spectrophotometric constants in aqueous solution. Solutions of iron weighing 0.0429 g, 0.1379 g, 0.2336 g, 0.3696 g, and 0.4356 g, from a stock solution containing $1.172 \cdot 10^{-6}$ g of iron per gram of solution were reduced with excess, iron free, hydroxylamine hydrochloride. A pH of 7 was provided by the addition of ammonium acetate after an excess of phenanthroline(III) in dilute hydrochloric acid had been added. Final dilution was made to 10 ml. A sample was placed in a quartz spectrophotometric cell having a 1 cm absorption path. The results are shown graphically in Fig. 1.

From the examination of Figure 1 the lower curve of which is the blank determination, and the successive superimposed curves represent the above listed increasing amounts of iron, the following values of the molecular extinction coefficient were calculated:

17106, 16000, 15990, 16568, and 16027.

The average molecular extinction coefficient is thus found to be 16340. The wave length of maximum absorption found was 510 mμ. A wave length of minimum absorption was shown in each case which varied slightly from the lowest to the highest iron concentration from 422 mμ to 415 mμ and indicated high absorption in the near ultra-violet. The BEER's law plot shows conformity over the range covered of 0.5 to 5 parts per million.

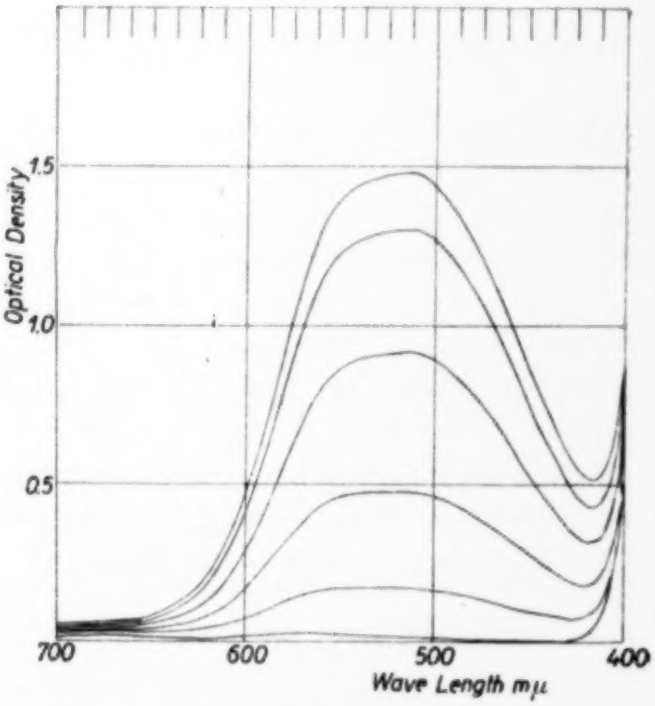

Fig. 1. 4,7-(3-Ethylaminopropylamino)-1,10-phenanthroline-Fe^{+2} complex in aqueous ammonia

Spectrophotometric constants in n*-hexyl alcohol solution.* Solutions of iron of the stock solution previously employed weighing 0.112 g, 0.226 g, 0.323 g, and 0.448 g were treated as indicated for the determinations just given and were treated with an excess of ammonia hydroxide and extracted once using *n*-hexyl alcohol and diluted to 10 ml using the same alcohol. The spectrophotometric examination of these solutions are shown in Fig. 2.

From the examination of Fig. 2, the lower curve of which is the blank determination and the successive superimposed curves represent the above

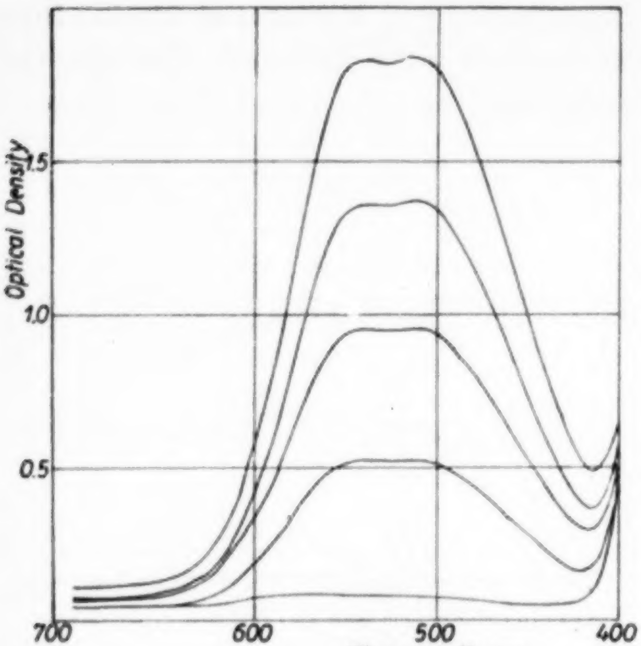

Fig. 2. 4,7-(3-Ethylaminopropylamino)-1,10-phenanthroline-Fe^{+2}complex in *n*-hexyl alcohol, $NH_4Ac + NH_4OH$

listed increasing concentrations of iron, the following molecular extinctions were calculated:

18933, 18554, 19032, and 18615. Average 18780.

The wave length of maximum absorption was found to be 510 mμ in duplication of that found for the aqueous solution of the ferroin complex. The wave length of minimum absorption was found to duplicate the values for aqueous solutions, (422 mμ to 415 mμ), and again there is indicated high absorption in the near ultraviolet. Conformity with BEER's law was again obtained over the same range of iron concentration. These solutions were re-examined after 66 hours of storage and no appreciable alteration in molecular extinction coefficient or wave length of maximum absorption was found.

Advantages in the use of 4,7-bis-(4-diethylaminopropylamino)- 1,10-phenanthroline. The chief advantages gained in the use of phenanthroline(III) in the application of the ferroin reaction are as follows:

Its high molecular extinction coefficient, (18780), is one of the highest so far found for a large number of substituted 1,10-phenanthrolines which could be employed in applying the ferroin reaction. (Bathophenanthroline[6], 22400).

Its ferrous complex, in the presence of ammonia is extractable in *n*-hexyl alcohol. This serves to concentrate the absorbing solution in a small volume of solvent and reduce, materially, the lower limit of measureable iron concentrations.

Its spectrophotometric absorption plateau (30-40 mμ wide) adapts this complexing agent to measurements employing filter photometers with advantages.

Color standards prepared from Fe(II) using phenanthroline(III) are unaltered in physical constants upon long standing.

COMPLEXING AGENT 4-(3-DIETHYLAMINOPROPYLAMINO)-1,10-PHENANTHROLINE AND THE FERROIN REACTION

The complexing agent, phenanthroline(II), has all the general characteristics of phenanthroline(III) with the exception that no green modification results when the ferroin reaction has been applied and the solution of the red complex is adjusted to pH 1 to 2.

References p. 56.

The same experimental procedures as those applied in the case of phenanthroline(III) for the *n*-hexyl alcohol extraction method were followed. The spectrophotometric curves obtained are shown in Fig. 3.

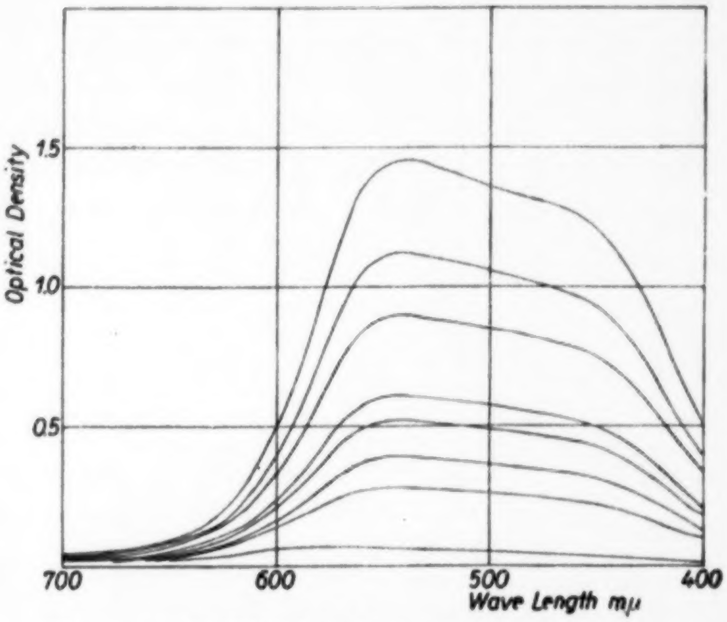

Fig. 3. 4-(3-Ethylaminopropylamino)-1,10-phenanthroline-Fe^{+2} complex in *n*-hexyl alcohol, $NH_4Ac + NH_4OH$

From the examination of Fig. 3 the following respective molecular extinction coefficients for the various concentrations of iron starting with lowest curve and proceeding to the highest (omitting the curve for the blank) were as follows:

12723, 12481, 12363, 12500,
13013, 12004, and 13440.
Average 12650.

The wave length of maximum absorption was found to be 543 mμ.

The alcohol extracted solutions were found to be inappreciably altered in color intensity after 93 hours storage under usual laboratory conditions. No minimum absorption in the visible range (400-700 mμ) was found as in the case of phenanthroline(III) ferrous complex solutions.

COMPLEXING AGENT 4,7-BIS-(4-DIETHYLAMINO-1-METHYLBUTYLAMINO)-1,10-PHENANTHROLINE. SPECTROPHOTOMETRIC STUDIES

The complexing agent, phenanthroline(I), has all the general characteristics of the previously described phenanthroline(III), including the formation of a green complex, from the ferroine red complex formed at pH 7, when the pH is lowered to 1 or 2. The red color is restored when the green complex is returned to a pH of seven. It is reasoned, by analogy to its similarity in structure to the ferrous complex of phenanthroline(III), that the ferroin reaction producing both red and green modifications are likewise tris-4,7-substituted 1,10-phenanthroline complex cations.

The same experimental procedures as those applied to in the case of phenanthroline(III) were followed in the study of phenanthroline(I). The plot of the spectrophotometric graphs for the *n*-hexyl alcohol extractions of the red ferroin reaction complex after addition of excess ammonia are shown in Fig. 4.

The following weighed portions of the same standard solution already described were taken ($1.172 \cdot 10^{-6}$ grams of Fe per gram).

References p. 56.

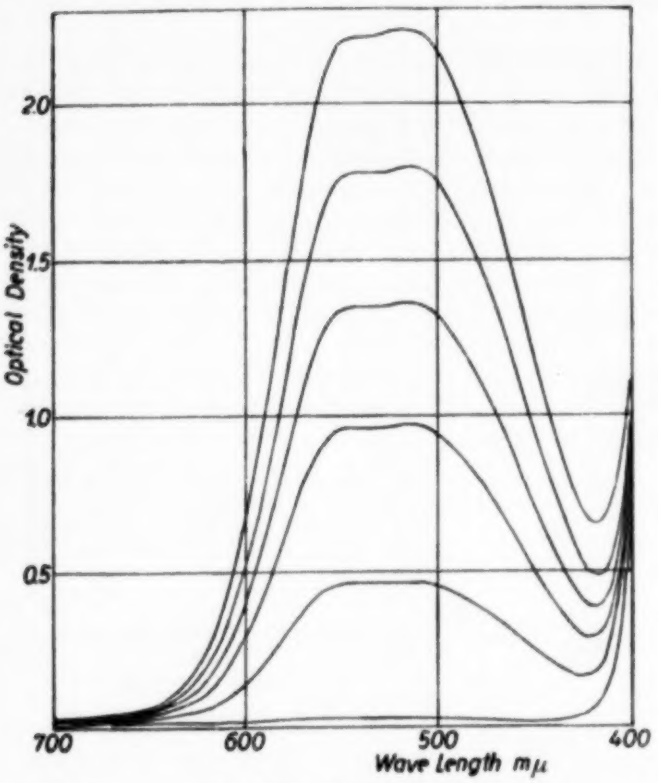

Fig. 4. 4,7-Bis-(4-diethylamino-1-methylbutylamino)-1,10-phenanthroline-Fe^{+2} complex in *n*-hexyl alcohol, $NH_4Ac + NH_4OH$

0.108 g, 0.216 g, 0.332 g, 0.442 g, and 0.549 g.

They were reduced by additions of excess hydroxylamine solutions, ammonium acetate used as buffer, and an excess of complexone phenanthroline(I) added. The resulting solution of the red complex was then treated by the addition of excess ammonium hydroxide and extracted using *n*-hexyl alcohol. The extraction solvent was diluted to 10 ml in a volumetric flask by the addition of *n*-hexyl alcohol and the spectrophotometric examination carried out as before. The graphs obtained, upon calculation, gave the following values for the molecular extinction. (The lowest curve graph in Fig. 4 is that of the blank for the reagents and the successively higher curves are in the order of increasing iron concentrations).

19194, 20760, 19133, 19094 and 19200. The average value excluding 20760 is 19156. The wave length of maximum absorption was found to be 519 mμ. The absorption spectra shows a minimum of 425 to 418 mμ. Strong absorption is indicated by the value to occur in the near ultraviolet region. The solutions used in the preparation of the graphs of Fig. 4 were stored under laboratory conditions for 44 hours and again subjected to spectrophotometric examination. No appreciable change was noted. The presence of a broad absorption maximum, (30-40 mμ) as for the case of phenanthroline(III) is again formed.

Solutions of iron were prepared as indicated above and the red complex formed by addition of phenanthroline(I) were subjected to spectrophotometric analysis without alcohol extraction. The same standard solution of iron as previously employed was sampled as follows:

0.1892 g, 0.2884 g, 0.3561 g, and 0.4655 g.

The resultant solutions were of 10 ml volume and gave the following molecular extinction coefficients:

17501, 17763, 17798, and 17751. Average 17703.

These data were taken from the graph of results shown in Fig. 5. The wave length of maximum absorption is found to be 510 mμ. The absorption

References p. 56.

spectra show a minimum at the same wave lengths as given in the case of the ferroin complex after *n*-hexyl alcohol extraction. BEER's law was found to be applicable over the range of iron concentrations applied. The lowest curve in Fig. 5 is that for the blank. The remaining graphs are in the order of increasing iron concentration.

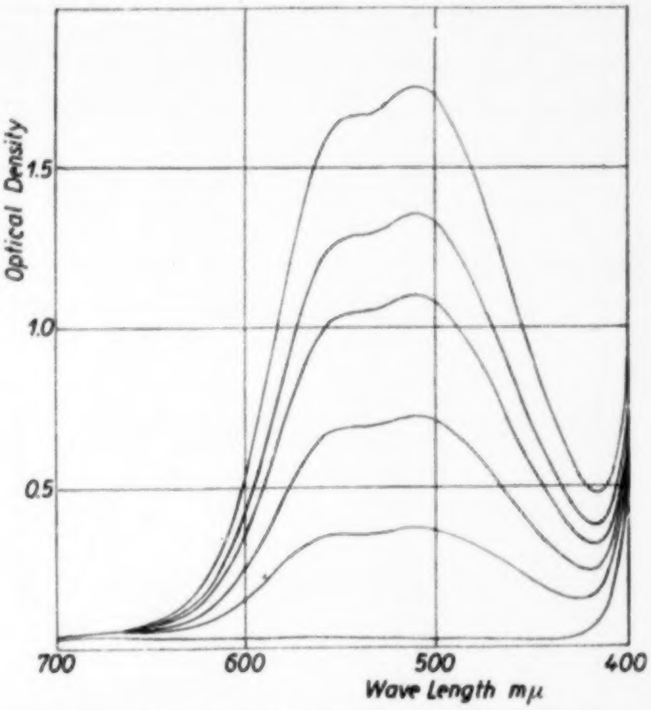

Fig. 5. 4,7-Bis-(diethylamino-1-methylbutylamino)-1,10-phenanthroline Fe^{+2} complex in aqueous ammonia, no buffer

DISCUSSION

The tabular data for the physical constants of the various complexing agents is given in Table II.

From the examination of the data in Table II it will be noted that of the phenanthrolines studied, the most sensitive reagent is phenanthroline(I) with two groups, (4-diethylamino-1-methylbutylamino), substituted in 1,10-phenanthroline(III), (3-diethylaminopropylamino) with the 4,7-positions of hydrogen replaced has but a slightly decreased molecular extinction coefficient (18780 as compared to 19156).

The extraction of the colored complex in *n*-hexyl alcohol results in a molecular extinction coefficient larger by 1453 units in the case of phenanthroline(I) and 2440 units with phenanthroline(III). The unsymmetrical phenanthroline (II) has a much increased wave length of maximum absorption, (543 mμ), than the corresponding symmetrical 4,7-derivative, (519 mμ). No plausible explanation of this unique distinction is readily at hand.

TABLE II

THE MOLECULAR EXTINCTION COEFFICIENTS AND THE WAVE LENGTH OF MAXIMUM ABSORPTION OF THE VARIOUS FERROIN REACTION PRODUCTS

	Molecular Extinction Coefficient		Wave Length Max. Absorption	
	Aq. Sol'n	*n*-Hexyl Al Sol'n	Aq. Sol'n mμ	*n*-Hexyl Al Sol'n mμ
Phenanthroline(I)	17703	19156	510	519
Phenanthroline(II)	—	12650	—	543
Phenanthroline(III)	16340	18780	5.0	510

References p. 56.

SUMMARY

Three modified 1,10-phenanthrolines containing dialkylaminoalkylamino groups in the 4- and 4,7-positions in place of hydrogen, have been described and their properties as complexing agents have been studied. The ferroin reaction of the new reagents results in complex cations which are soluble in *n*-hexyl alcohol only after the addition of ammonium hydroxide. The molecular extinction coefficients of these ferroin reaction complexes are high, above 19000 in the case of 4,7-bis-(4-diethylamino-1-methylbutylamino)-1,10-phenanthroline. The aqueous solutions of the same complex cations have significantly lower molecular extinction coefficients than their extracted alcohol solutions. In the absence of ammonium hydroxide the aqueous solution of the ferroin complexes are markedly unstable. The ferroin complexes are tris-phenanthroline cations, stable upon long standing in the presence of excess ammonia. There are red and green colored complexes depending upon the pH of formation, the color being reversible upon increasing pH from 2 to 6 in the manner of a pH indicator.

Possible analytical applications of the new modified 1,10-phenanthrolines have been suggested.

RÉSUMÉ

On décrit trois dérivés de la 1,10-phénanthroline renfermant les groupements dialcylaminoalcylamino en positions 4 et 4,7. Leurs propriétés d'agents complexants ont été étudiées. La réaction de la ferroïne avec ces nouveaux réactifs donne des cations complexes solubles dans l'alcool *n*-hexylique, après addition d'hydroxyde d'ammonium. Les coefficients d'extinction moléculaires de ces complexes sont élevés, plus grands que 19000 dans le cas de la 4,7 bis (4-diéthylamino-1-méthylbutylamino)-1,10-phénanthroline. Les solutions aqueuses de ces cations complexes ont des coefficients d'extinction plus faibles que les extraits alcooliques. En l'absence d'hydroxyde d'ammonium, la solution aqueuse des complexes ,,ferroïne" sont très instables. Par contre, en présence d'un excès d'ammoniaque ces complexes (cations tri-phénanthroline) sont très stables. Ils sont rouges et verts suivant le pH; ils virent entre les pH 2 et 6, comme un indicateur.

Quelques applications analytiques de ces nouveaux dérivés de la 1,10-phénanthroline sont proposées.

ZUSAMMENFASSUNG

Drei substituierte 1,10-Phenanthroline, welche in Stellung 4 und 4,7 Dialkylaminoalkylamino-Gruppen enthalten und ihre Eigenschaften als Komplexbildner werden beschrieben. Die Ferroin-Reaktion der neuen Reagentien komplexe Kationen welche erst nach Zugabe von Ammoniumhydroxyd in *n*-hexylalkohol löslich sind. Die molekularen Extinktionskoeffizienten dieser Komplexe sind hoch, oberhalb 19,000 im Falle von 4,7-bis(4-Diäthylamino-1-Methylbutylamino)-1,10-Phenanthrolin. Wässrige Lösungen derselben komplexen Kationen haben bedeutend niedrigere molekulare Extinktionskoeffizienten als ihre extrahierte alkoholische Lösungen. In Abwesenheit von Ammoniumhydroxyd sind die wässrige Lösungen der Ferroinkomplexe sehr unbeständig. Die Ferroinkomplexe enthalten drei Phenanthrolinmoleküle; sie sind sehr beständig in Gegenwart von überschüssigem Ammoniak. Je nach dem pH sind sie rot oder grün. Zwischen pH 2 und 6 ist der Farbumschlag wie bei einem pH-Indikator reversibel. Analytische Anwendungen der neuen Verbindungen werden vorgeschlagen.

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CONTRIBUTION À L'ÉTUDE DES MÉTHODES DE DOSAGES ÉLECTROTITRIMÉTRIQUES

par

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Durant ces dernières années, de nombreux travaux, particulièrement ceux de CHARLOT *et coll.* [1 à 6], de FURMAN *et coll.* [7, 8] et de DELAHAY[9], ont montré l'importance de la connaissance des courbes de polarisation pour l'interprétation et l'utilisation judicieuse des méthodes de dosage électrométriques (potentiométrie, ampérométrie, polarographie).

Dans mon laboratoire, nous avons également eu l'occasion d'attirer l'attention sur les relations qui existent entre ces différentes méthodes en faisant appel aux courbes de polarisation et ces considérations ont conduit à la mise au point de plusieurs dosages ampérométriques simplifiés [10 à 12].

L'étude quantitative de ces différentes méthodes électrotitrimétriques, basée sur les courbes de polarisation, a été faite par REILLEY, COOKE ET FURMAN[7] dans le cas particulier des réactions d'électrodes réversibles, et ces considérations les ont conduits à une nouvelle variante de méthode électrotitrimétrique appelée „titration polarographique dérivée"[8].

Il nous avait paru, à la lecture de cet article, que le cas des vagues polarographiques réversibles envisagé par ces auteurs était d'application extrêmement restreinte et qu'une méthode d'étude plus générale englobant les courbes de polarisation réversibles serait souhaitable.*

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* Lors du Congrès international de chimie analytique tenu à Oxford au mois de septembre, mon collègue G. CHARLOT m'a signalé qu'ils avaient fait dans son laboratoire, une étude générale sur cette question, suivant les mêmes lignes et que son collaborateur R. GAUGUIN venait de publier la première partie du travail (voir R. GAUGUIN, *Anal. Chim. Acta*, 7 (1952) 105).

Les discussions que j'ai eu l'occasion d'avoir avec MM. CHARLOT, GAUGUIN ET COURSIER ainsi que la lecture du mémoire cité m'ont donné l'impression que, si nous avons l'un et l'autre abordé l'étude du même problème par la même méthode de principe, celle de GAUGUIN est encore plus générale et l'application qu'il en a faite est encore plus étendue que celle que nous en avions faite jusqu'à présent.

Il nous a paru néanmoins utile de publier cette note, en passant très rapidement sur les équations générales qui sont étudiées très en détail et de façon plus générale dans la publication de GAUGUIN et en considérant l'application particulière au cas des méthodes du „dead-stop end-point" et „dérivée" de REILLEY, COOKE ET FURMAN.

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Nous établirons succinctement une expression assez générale des courbes de polarisation tenant compte des vitesses de réactions et des phénomènes de diffusion et nous en envisagerons l'application particulière à la méthode du „dead stop end-point" et à la méthode dérivée de REILLEY, COOKE ET FURMAN.

ÉQUATION DE LA COURBE DE POLARISATION D'UN COUPLE OXYDO-RÉDUCTEUR

Nous nous sommes inspirés d'un article de EYRING, MARKER ET KWOOH[13].

En présence d'un excès d'électrolyte support (qui permet de négliger le courant de migration du système oxydo-réducteur étudié), la courbe de polarisation d'un système oxydo-réducteur (1)

$$\mathrm{Ox} + \mathrm{ne} \rightleftarrows \mathrm{Red} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

établie à partir de la cinétique de la réaction est donnée par l'équation suivante:

$$i = k_1\,[\mathrm{Ox}]_0\,\mathrm{e}^{-a\frac{nF}{RT}E} - k_2\,[\mathrm{Red}]_0\,\mathrm{e}^{+(1-a)\cdot\frac{nF}{RT}E} \quad \ldots\ldots \quad (2)$$

i: densité du courant d'électrolyse (+: bilan total est une réduction).
E: potentiel de la microélectrode. (+ du côté du système très oxydant).
$[\mathrm{Ox}]_0$, $[\mathrm{Red}]_0$: activités au voisinage immédiat de l'électrode.
$[\mathrm{Ox}]$, $[\mathrm{Red}]$: activités au sein de la solution.
k_1, k_2: constantes proportionnelles aux constantes de vitesses de réduction et d'oxydation.
a: coefficient d'activation.

En introduisant dans l'équation (2), les équations de diffusion suivantes:

$$i = K_{\mathrm{ox}}\{[\mathrm{Ox}] - [\mathrm{Ox}]_0\} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$
$$i = -K_{\mathrm{red}}\{[\mathrm{Red}] - [\mathrm{Red}]_0\} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

on obtient l'équation de la courbe de polarisation tenant compte des polarisations chimiques et de concentration:

$$i = \frac{[\mathrm{Ox}] - [\mathrm{Red}]\,\mathrm{e}^{\frac{nF}{RT}(E-E_0)}}{\frac{1}{k_1}\,\mathrm{e}^{\frac{na\,F}{RT}E} + \frac{1}{K_{\mathrm{ox}}} + \frac{1}{K_{\mathrm{red}}}\,\mathrm{e}^{\frac{nE}{RT}(E-E_0)}} \quad \ldots\ldots \quad (5)$$

dans laquelle $E_0 = \frac{RT}{nF}\ln\frac{k_1}{k_2}$ (6) est le potentiel normal d'oxydo-réduction.

En pratique, cette équation est limitée aux systèmes qui tombent dans la zone des potentiels définie par la courbe de polarisation de l'eau (voir COURSIER[6]).

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Cas particuliers

La formule générale (5) se simplifie dans les cas particuliers qui peuvent se présenter:

a) Système réversible: $$\frac{1}{k_1}\,e^{\frac{\alpha\, n F}{RT}E} \ll \frac{1}{K_{ox}} + \frac{1}{K_{red}}\,e^{\frac{nF}{RT}(E-E_0)} \quad \ldots\ldots\ldots \quad (7)$$

La formule (5) se ramène à l'équation classique polarographique de la vague d'un système oxydo-réducteur réversible:

$$E = E_0 + \frac{RT}{nF}\ln\frac{K_{red}}{K_{ox}} + \frac{RT}{nF}.\ln\frac{(id)_c - i}{i - (id)_a} \quad \ldots\ldots\ldots \quad (8)$$

dans laquelle $(id)_c = K_{ox}\,[\mathrm{Ox}]$: (courant limite de diffusion)
$(id)_a = -K_{red}\,[\mathrm{Red}]$: (courant limite de diffusion)

b) Système très irréversible: $$\frac{1}{k_1}\,e^{\frac{\alpha\, n F}{RT}E} \gg \frac{1}{K_{ox}} + \frac{1}{K_{red}}\,e^{\frac{nF}{RT}(E-E_0)} \quad \ldots\ldots \quad (9)$$

La formule (5) se ramène à l'équation suivante:

$$i = k_1\,[\mathrm{Ox}]\,e^{-\frac{\alpha\, n F}{RT}E} - k_2\,[\mathrm{Red}]\,e^{\frac{(1-\alpha)\, nF}{RT}E} \quad \ldots\ldots \quad (10)$$

La courbe de polarisation est uniquement contrôlée par la vitesse de réaction. Il va de soi que cette équation ne sera applicable que dans le cas de réactions irréversibles et pour des densités de courant suffisamment faibles pour que la polarisation de concentration soit négligeable — c'est à dire au voisinage immédiat du point d'intersection de la courbe avec l'axe des courants.

c) Courbe de réduction d'un système oxydo-réducteur très irréversible.

Lorsque $E \ll E_0$, l'équation (5) se réduit à

$$i = \frac{[\mathrm{Ox}]}{\frac{1}{k_1}\,e^{\frac{\alpha\, n F}{RT}E} + \frac{1}{K_{ox}}} \quad \ldots\ldots\ldots\ldots\ldots \quad (11)$$

d) Courbe d'oxydation d'un système oxydo-réducteur très irréversible

$$i = \frac{[\mathrm{Red}]}{\frac{1}{k_2}\,e^{\frac{(1-\alpha)\, nF}{RT}E} + \frac{1}{K_{red}}} \quad \ldots\ldots\ldots\ldots \quad (12)$$

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On peut délimiter le domaine d'application des différentes formules approchées, pour les systèmes irréversibles, dans la Fig. 1.

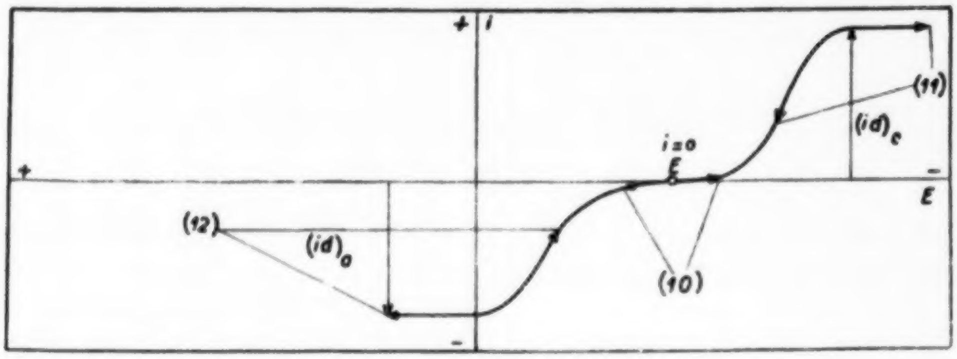

Fig. 1. Domaine d'application des formules (10), (11) et (12) pour les systèmes irréversibles.

Application aux méthodes électrotitrimétriques „dead-stop end-point" et „dérivée"

DELAHAY[9] a le premier montré qualitativement comment les courbes de titrages obtenues par la méthode de FOULK ET BAWDEN peuvent s'interpréter à partir des courbes de polarisation des systèmes intervenant dans la réaction de titrage.

REILLEY, COOKE ET FURMAN[7, 8] ont donné une interprétation quantitative des courbes électrotitrimétriques du „dead-stop end-point" et „dérivée" dans le cas particulier où

1. les deux systèmes d'un titrage oxydo-réducteur se comportent réversiblement à l'électrode indicatrice.
2. la différence de potentiel constante appliquée (dead-stop end-point) ou le courant constant de polarisation (méthode dérivée) sont *très faibles*. Dans ce cas, la grandeur mesurée au cours du titrage représente soit $\left(\frac{\delta i}{\delta E}\right)_{i=0}$ soit $\left(\frac{\delta E}{\delta i}\right)_{i=0}$

Calcul de $\left(\frac{\delta i}{\delta E}\right)_{i=0}$ *pour un couple oxydo-réducteur à courbe de polarisation contrôlée uniquement par la vitesse de réaction.*

En introduisant dans l'équation (10) la proportion de forme réduite,

$$\left(x = \frac{[\mathrm{Red}]}{[\mathrm{Red}] + [\mathrm{Ox}]}\right)$$

C'est à dire $[\mathrm{Ox}] = C_0\,(1-x)$ $[\mathrm{Red}] = C_0 x$ (13)

on obtient comme équation de la courbe de polarisation, au voisinage de $i = 0$,

$$i = k_1\,C_0\,(1-x)\,\mathrm{e}^{-\frac{\alpha\,n\,F}{RT}E} - k_2\,C_0\,x\,\mathrm{e}^{\frac{(1-\alpha)\,nF}{RT}E} \quad \ldots\ldots \quad (14)$$

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Par dérivation de l'équation (14), on trouve que

$$\left(\frac{\delta i}{\delta E}\right)_{i=0}^{\text{irr.}} = -\frac{nF}{RT}C_0\,[k_1\,(1-x)]^{1-a}\,[k_2x]^{a} \quad \ldots\ldots\ldots \quad (15)$$

REILLEY, COOKE ET FURMAN ont montré que, dans le cas d'un couple oxydo-réducteur réversible,

$$\left(\frac{\delta i}{\delta E}\right)_{i=0}^{\text{rev.}} = -\frac{nF}{RT}C_0\,\frac{1}{K_{\text{ox}}\,(1-x)} + \frac{1}{K_{\text{red}}\,x} \quad \ldots\ldots\ldots \quad (16)$$

Il est aisé de montrer que

$$\left(\frac{\delta i}{\delta E}\right)_{i=0}^{\text{irr.}} \leqslant \left(\frac{\delta i}{\delta E}\right)_{i=0}^{\text{rev.}} \quad \ldots\ldots\ldots\ldots\ldots \quad (17)$$

quelle que soit la valeur de x.

En effet, nous avons vu que la condition de validité de l'équation (14) est que

$$\frac{1}{k_1}\,e^{\frac{a\,nF}{RT}E} \geqslant \frac{1}{K_{\text{ox}}} + \frac{1}{K_{\text{red}}}\,e^{\frac{nF}{RT}(E-E_0)}$$

Cette condition doit donc aussi être réalisée pour $E_{i=0}$. c'est à dire que

$$\frac{1}{k_1}\,e^{\frac{a\,nF}{RT}E_{i=0}} \geqslant \frac{1}{K_{\text{ox}}} + \frac{1}{K_{\text{red}}}\,e^{\frac{nF}{RT}(E-E_0)_{i=0}} \quad \ldots\ldots\ldots \quad (18)$$

Or

$$e^{\frac{nF}{RT}E_{i=0}} = \frac{k_1\,(1-x)}{k_2\,x} \text{ et } e^{\frac{nF}{RT}E_0} = \frac{k_1}{k_2} \quad \ldots\ldots\ldots \quad (19)$$

Il en résulte que

$$\frac{k_1^{a-1}}{k_2^{a}}\,\frac{(1-x)^a}{x^a} \geqslant \frac{1}{K_{\text{ox}}} + \frac{1}{K_{\text{red}}}\,\frac{1-x}{x} \quad \ldots\ldots\ldots\ldots \quad (20)$$

Cette expression (20) peut encore se mettre sour la forme suivante

$$\frac{1}{k_1^{1-a}\,k_2^{a}\,x^a\,(1-x)^{1-a}} \geqslant \frac{1}{K_{\text{ox}}\,(1-x)} + \frac{1}{K_{\text{red}}\,x} \quad \ldots\ldots \quad (21)$$

Si nous comparons l'expression (21) aux deux équations (15) et (16), nous voyons que l'inégalité (21) revient à dire que

$$\left|\left(\frac{\delta i}{\delta E}\right)_{i=0}^{\text{irr.}}\right| \leqslant \left|\left(\frac{\delta i}{\delta E}\right)_{i=0}^{\text{rev.}}\right| \quad \text{C.Q.F.D.}$$

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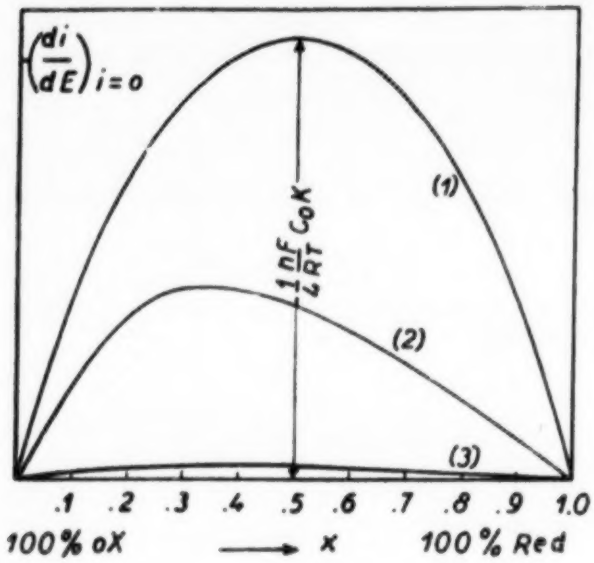

Fig. 2.
Méthode du „dead-stop end-point"

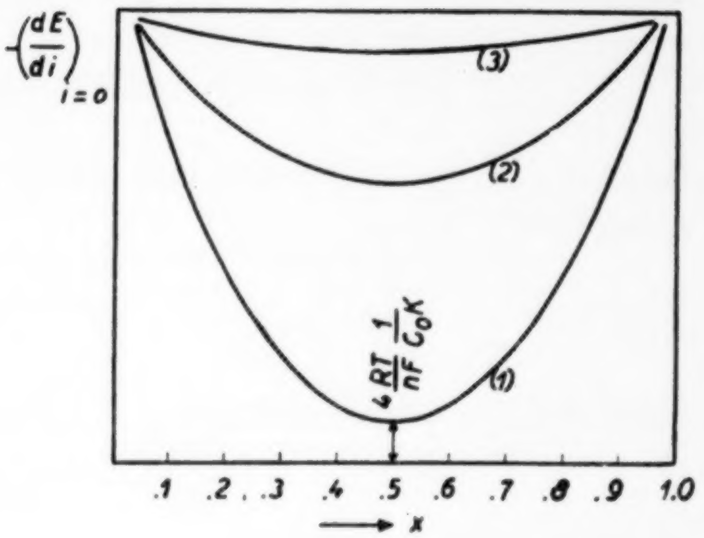

Fig. 3.
Méthode „dérivée"

(1) couple oxydo-réducteur réversible ($K_{\text{ox}} = K_{\text{red}} = K$)
(2) couple oxydo-réducteur sujet à la polarisation chimique et à la polarisation de concentration
(3) couple oxydo-réducteur très irréversible

Les Figs. 2 et 3 représentent schématiquement, en fonction de $x = \frac{[\text{Red}]}{[\text{Ox}] + [\text{Red}]}$, les variations de $\left(\frac{\delta i}{\delta E}\right)_{i=0}$, ainsi que de son inverse $\left(\frac{\delta E}{\delta i}\right)_{i=0}$, données par les formules (16) et 15) ainsi que celles d'un système où le phénomène à l'électrode est contrôlé à la fois par la vitesse de réaction et par la diffusion ($a \neq 0{,}5$).

Courbes de titrage

Lorsqu'on titre un oxydant Ox_1 par un réducteur Red_2, il suffit de considérer séparément les courbes $\left(\frac{\delta i}{\delta E}\right)_{i=0}$ où $\left(\frac{\delta E}{\delta i}\right)_{i=0}$ des deux couples oxydo-réducteurs

$$\text{Ox}_1 + ne \rightleftarrows \text{Red}_1$$
$$\text{Ox}_2 + ne \rightleftarrows \text{Red}_2$$

pour connaître l'allure générale de la courbe de titrage.

Il va de soi que, par suite de l'existence d'équilibre $\text{Ox}_1 + \text{Red}_2 \rightleftarrows \text{Ox}_2 + \text{Red}_1$. ces courbes ne tendent pas vers une valeur nulle ou infinie au point équivalent.

Ainsi, par exemple, dans le cas d'un système réversible, il est facile de montrer qu'au point équivalent

$$\left(\frac{\delta i}{\delta E}\right)_{i=0}^{\text{équiv.}} \cong -\frac{nF}{RT}\, C_0\, K \sqrt{K} \quad \ldots\ldots\ldots\ldots \quad (22)$$

$$\text{où } K = \frac{[\text{Ox}_1]\,[\text{Red}_2]}{[\text{Ox}_2]\,[\text{Red}_1]} \quad \ldots\ldots\ldots\ldots\ldots \quad (23)$$

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La Fig. 4 schématise les courbes de titrage au voisinage du point équivalent que l'on est en droit d'attendre avec certaines combinaisons de systèmes oxydo-réducteurs (allant du système réversible au système contrôlé uniquement par la vitesse de la réaction).

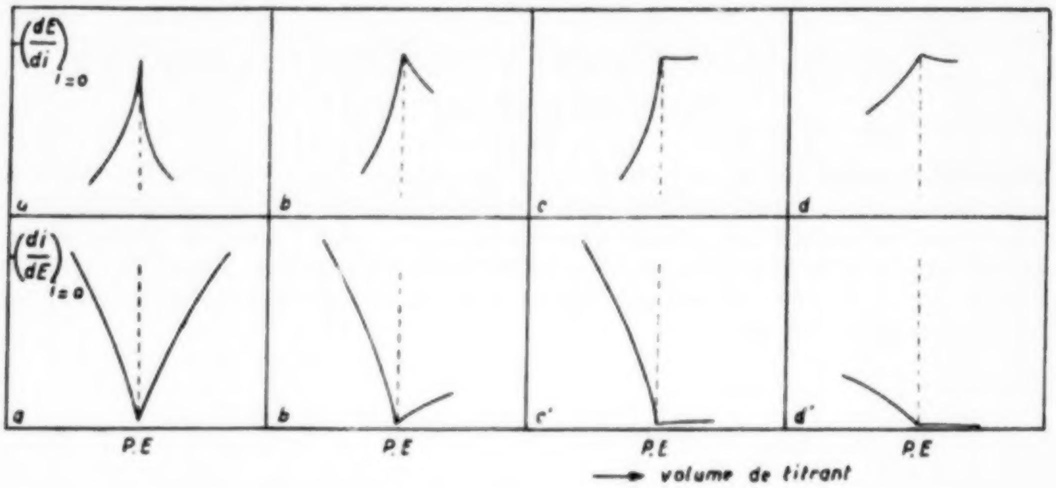

Fig. 4. Courbes de titrage: méthode ,,dérivée" de REILLEY, COOKE ET FURMAN (a, b, c, d); méthode du ,,dead-stop end-point" de FOULK ET BAWDEN (a', b', c', d').

(a) deux couples oxydo-réducteurs réversibles
(b) un couple oxydo-réducteur réversible titré par un couple présentant une certaine irréversibilité
(c) un couple oxydo-réducteur réversible titré par un couple très irréversible
(d) un couple oxydo-réducteur faiblement irréversible titré par un couple très irréversible

Si l'on se reporte aux données expérimentales récentes sur la question[14, 15, 8], on constate que les prévisions sont parfaitement réalisées et que l'interprétation des phénomènes est satisfaisante.

L'équation générale (5) de la courbe de polarisation peut évidemment servir, en principe, pour discuter quantitativement les autres méthodes de titrage électrométriques (potentiométrie sous courant nul ou constant, sous résistance constante, ampérométrie sous voltage ou résistance constant), d'une façon analogue à celle utilisée par REILLEY, COOKE ET FURMAN dans le cas particulier des systèmes réversibles; mais, on se heurte souvent à des difficultés mathématiques sérieuses et il est probable que des méthodes graphiques seraient plus indiquées.

RÉSUMÉ

L'auteur établit une équation générale de la courbe de polarisation d'un couple oxydo-réducteur tenant compte de la cinétique des réactions et de la polarisation de concentration et il en montre l'application dans l'interprétation des courbes de titrage obtenues par la méthode du ,,dead-stop end-point" de FOULK ET BAWDEN et par la méthode dérivée de REILLEY COOKE ET FURMAN.

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SUMMARY

The author establishes a general equation for the polarisation curve of an oxidation-reduction system taking into account the kinetics of reactions and concentration polarisation, and shows how it can be applied to the interpretation of titration curves obtained by the dead-stop end-point method of Foulk and Bawden and by the derivative method of Reilley, Cooke and Furman.

ZUSAMMENFASSUNG

Der Verfasser stellt eine allgemeine Gleichung der Polarisationskurve eines Oxydations-Reduktionspaares-Systemes fest, indem er dabei die Reaktionskinetik und die Konzentrationspolarisation berücksichtigt, und beweist deren Anwendung bei der Ausdeutung der Analysenkurven die man durch die ,,dead stop end point" Methode von Foulk und Bawden nebst der Derivative Methode von Reilley, Cooke und Furman erhält.

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UTILISATION DES COURBES DE POLARISATION DANS LES DOSAGES ÉLECTROCHIMIQUES

IV. AMPÉROMÉTRIE À TENSION CONSTANTE

par

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Au cours d'un dosage par voie chimique, on peut plonger dans la solution deux électrodes entre lesquelles on effectue, sous tension constante, une électrolyse avec un courant suffisamment petit pour que la consommation de réactif soit négligeable. Dans des conditions particulières, la courbe „ampérométrique", c'est-à-dire la courbe de variation de l'intensité d'électrolyse en fonction de la quantité de réactif ajouté présente un point singulier au point équivalent et permet de le déceler.

Après avoir précisé les propriétés générales des courbes de polarisation[1], nous avons étudié les déformations d'une telle courbe au cours d'un dosage, puis nous avons appliqué ces résultats à la potentiométrie à intensité constante[2] et à la coulométrie à intensité constante[3].

Considérant la tension d'électrolyse comme constante, nous allons utiliser ces mêmes résultats pour essayer de préciser les conditions d'utilisation de l'ampérométrie avec ou sans électrode de référence ("dead-stop end-point").

A. AMPÉROMÉTRIE AVEC UNE SEULE ÉLECTRODE INDICATRICE

L'électrolyse est effectuée entre une électrode indicatrice et une électrode de référence, laquelle garde un potentiel constant indépendant de la densité du courant qui la traverse (voir page 71).

DOSAGE PAR PRÉCIPITATION

Comme nous l'avons fait pour la potentiométrie, envisageons d'abord le cas simple où un seul des corps participant à la réaction de dosage est électroactif. Supposons que ce corps soit un réducteur que nous représentons par Red.

Réaction de dosage. Au réducteur Red, nous ajoutons un réactif titrant qui le précipite quantitativement. Si c_0 est la concentration initiale du réducteur on peut représenter par $c_0(1-x)$ sa concentration au cours du dosage. Le point équivalent correspond à $x = 1$, $|\mathrm{Red}| = 0$.

Réaction indicatrice. Nous supposons qu'à l'anode l'oxydation du réducteur peut être représentée par

$$\mathrm{Red} \rightarrow \mathrm{Ox} + \mathrm{e}.$$

Variation de l'intensité d'électrolyse. Le potentiel de l'électrode de référence et la tension appliquée étant constants, le potentiel de l'électrode indicatrice est également constant.

Dans le cas envisagé ($|\mathrm{Ox}| = 0$, nombre d'électrons échangés par Red égal à 1) l'équation de la courbe de polarisation[1] s'écrit

$$I = \frac{k\ F\ |\mathrm{Red}|\ \mathrm{e}^{\frac{\beta F}{RT}E}}{1 + \frac{k}{k_d}\mathrm{e}^{\frac{\beta F}{RT}E} + \frac{k'}{k_d'}\mathrm{e}^{-\frac{\alpha F}{RT}E}} \quad \ldots\ldots\ldots\ldots \quad (1)$$

si la solution contient un excès d'électrolyte indifférent. Lorsque le potentiel E est constant, en remplaçant $|\mathrm{Red}|$ par sa valeur $c_0\,(1-x)$, l'équation se réduit à

$$I = I_0\ (1-x) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2).$$

où I_0 est la densité du courant dans les conditions initiales ($x = 0$):

$$I_0 = \frac{k\ F\ c_0\ \mathrm{e}^{\frac{\beta F}{RT}E}}{1 + \frac{k}{k_d}\mathrm{e}^{\frac{\beta F}{RT}E} + \frac{k'}{k_d'}\mathrm{e}^{-\frac{\alpha F}{RT}E}} \quad \ldots\ldots\ldots \quad (3)$$

Ces équations sont valables avant le point équivalent. Au-delà du point équivalent la concentration du réducteur est nulle et $I = 0$.

La courbe est formée de deux droites (Fig. 1) comme chaque fois que l'on suit au cours d'un dosage une fonction linéaire des concentrations. Elle peut se déduire de l'ensemble des courbes de polarisation $i = f(E)$ à différentes valeurs du paramètre x, dont on considère l'intersection avec la verticale $\alpha\beta$, d'abscisse E_A (Fig. 2).

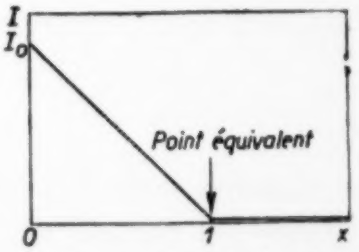

Fig. 1. Précipitation d'un réducteur électroactif par un composé inerte.

L'ampérométrie „polarographique" correspond au cas où la droite $\alpha\beta$ rencontre le palier de diffusion des courbes de polarisation. Cette condition n'est donc pas obligatoire pour un dosage.

Influence d'un système oxydo-réducteur parasite. Supposons que la solution contienne un excès d'un oxydant ou d'un réducteur qui ne participe pas à la réaction de dosage. Au potentiel imposé à l'électrode indicatrice, ce système s'oxyde ou se réduit avec une intensité constante, qui s'ajoute algébriquement à la densité d'électrolyse du corps dosé Red. La courbe de dosage est donc — en principe — simplement translatée verticalement d'une quantité constante.

Le solvant en général et l'eau en particulier, peuvent jouer le rôle de système oxydo-réducteur parasite.

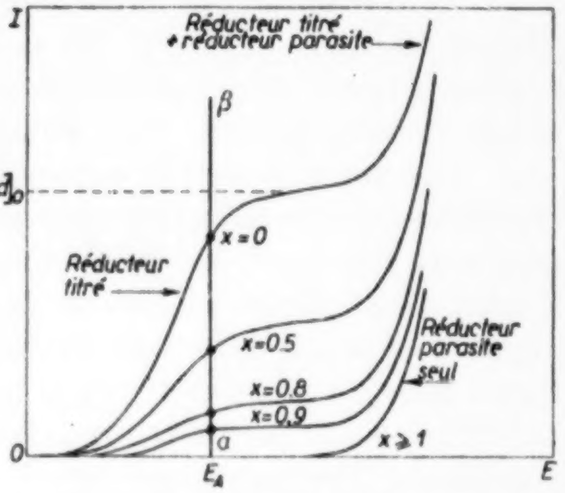

Fig. 2. Relation entre la courbe de dosage et les courbes de polarisation correspondant à différentes valeurs de x.

Influence des autres facteurs sur la courbe de dosage

1. Nous avons supposé qu'un excès d'électrolyte indifférent rendait nul le nombre de transport du corps dosé. S'il n'en est pas ainsi, l'équation (1) doit être remplacée[1] par

$$I = \frac{k\ F\ |\mathrm{Red}|\ \mathrm{e}^{\frac{\beta F}{RT}E}}{1 + \frac{k}{k_d}\left(1 + \frac{t}{z}\right)\mathrm{e}^{\frac{\beta F}{RT}E} + \frac{k'}{k_d'}\mathrm{e}^{-\frac{\alpha F}{RT}E}}$$

où t et z sont respectivement le nombre de transport du réducteur et sa charge, comptée algébriquement.

Dans ce cas, non seulement Red mais aussi t varient avec x, le premier tronçon de la courbe de dosage n'est plus une droite. La détection du point équivalent devient plus difficile et même impossible si la réaction de dosage est, en outre, non rigoureusement quantitative.

Un excès d'électrolyte indifférent égal à 100 fois la concentration du corps à doser rend le terme $\frac{t}{z}$, inférieur ou égal à 1 %, et pratiquement négligeable[1].

2. Nous avons supposé en outre que la réaction était rigoureusement quantitative. Ceci est réalisé avec une plus ou moins bonne approximation, et au voisi-

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nage du point équivalent la courbe réelle peut présenter un arrondi plus ou moins étendu. Les prolongements des parties rectilignes de la courbe se coupent au voisinage du point équivalent si la réaction est suffisamment quantitative[4].

3. Nous avons admis implicitement que le volume de la solution ne changeait pas par addition du réactif. On se rapproche de cette condition en prenant une solution titrante plus concentrée que la solution titrée. Des corrections plus ou moins valables peuvent être utilisées[4].

4. Lorsque le potentiel imposé à l'électrode croît — dans le cas choisi, de la précipitation d'un réducteur — la pente de la droite AB décroît (algébriquement), puis reste constante, lorsqu'au potentiel imposé le courant limite de diffusion est atteint. Généralement lorsqu'on augmente trop le potentiel on se trouve sur la vague d'un autre réducteur, la courbe de dosage, en principe, garde la même forme mais est translatée vers le haut. C'est évidemment dans la zone du palier de diffusion que les variations accidentelles de potentiel ont le moins de répercussion sur l'intensité mesurée.

5. En augmentant la surface de l'électrode les intensités observées sont plus grandes.

6. En agitant la solution ou l'électrode, les coefficients k_d et k_d' augmentent et la densité de courant pour un même potentiel est plus élevée qu'en l'absence d'agitation. Il faut d'ailleurs remarquer, que le palier de diffusion est également atteint pour des potentiels plus élevés (dans le cas de l'oxydation d'un réducteur).

On constate souvent que les intensités mesurées sont plus stables qu'avec une électrode stationnaire. L'agitation doit être régulière pour que les coefficients k_d et k_d' soient constants.

AUTRES TYPES DE RÉACTION DE PRÉCIPITATION

D'une manière générale, à un potentiel imposé, chaque oxydant ou réducteur pris isolément réagit à l'électrode en donnant une densité de courant proportionnelle à sa concentration. Nous avons vu[1] qu'en présence d'un électrolyte indifférent, ces densités sont en principe additives: la densité de courant observée est la somme de ces densités partielles.

Le corps titré et le corps titrant ont les concentrations suivantes (pour une réaction quantitative, en supposant tous les coefficients égaux à 1)

	Avant le P.E	P.E	Après le P.E
corps titré	$c_0(1-x)$	0	0
corps titrant	0	0	$c_0(x-1)$

La densité observée est donc

$I = I_{1,0}\ (1-x)$ avant le point équivalent,
$I = 0$ au point équivalent,
$I = I_{2,0}\ (x-1)$ après le point équivalent.

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$I_{1,0}$ et $I_{2,0}$ sont les densités du courant dû au corps titré et au corps titrant, lorsque ceux-ci ont la concentration c_0.

Ces coefficients sont de la forme (1)

$$I_0 = \frac{k\,F\,n_T\,e^{\frac{\beta n F}{RT}E}}{1 + \frac{k}{k_d}\,e^{\frac{\beta n F}{RT}E} + \frac{k'}{k_d'}\,e^{-\frac{\alpha n' F}{RT}E}}$$

ou
$$I_0 = \frac{-k'\,F\,n_T\,e^{-\frac{\alpha n' F}{RT}E}}{1 + \frac{k}{k_d}\,e^{\frac{\beta n F}{RT}E} + \frac{k'}{k_d'}\,e^{-\frac{\alpha n' F}{RT}E}}$$

Dans ces équations n_T est le nombre d'électrons échangés à l'électrode par le composé correspondant, n le nombre d'électrons échangés dans la réaction partielle la plus lente. La première s'applique à un réducteur, la deuxième à un oxydant.

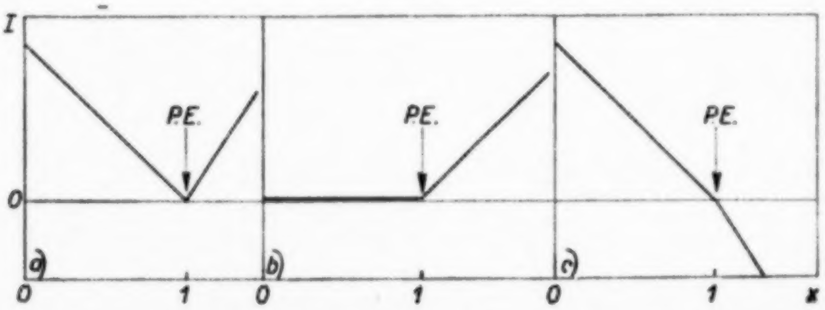

Fig. 3. Différentes formes des courbes de dosage:
a) précipitation d'un réducteur électroactif par un autre réducteur électroactif.
b) précipitation d'un corps inerte par un réducteur électroactif.
c) précipitation d'un réducteur par un oxydant.

Ces coefficients prennent des valeurs différentes selon le potentiel imposé. On est ainsi ramené au cas des courbes linéaires de dosage en général[1]. La figure 3 montre quelques types de courbes possibles.

On peut remarquer sur toutes ces courbes un changement de pente au point équivalent, par ailleurs l'ordonnée en ce point est nulle, en l'absence de courant résiduel.

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RÉACTIONS D'OXYDO-REDUCTION

Le problème peut être traité de façon analogue. Supposons que la réaction soit

$$\mathrm{Red}_1 + \mathrm{Ox}_2 \rightleftarrows \mathrm{Red}_2 + \mathrm{Ox}_1$$

Dans le cas d'une réaction quantitative et avec les mêmes notations, les concentrations des différents corps varient maintenant de la façon suivante:

	Avant le P.E	P.E	Après le P.E
$\lvert\mathrm{Red}_1\rvert$	$c_0(1-x)$	0	0
$\lvert\mathrm{Ox}_1\rvert$	xc_0	c_0	c_0
$\lvert\mathrm{Red}_2\rvert$	xc_0	c_0	c_0
$\lvert\mathrm{Ox}_2\rvert$	0	0	$c_0(x-1)$

Nous pouvons écrire comme précédemment, en additionnant les densités partielles

$I = I_{0,1} + (I_{0,1}' + I_{0,2} - I_{0,1})x$ avant le point équivalent
$I = I_{0,1}' + I_{0,2}$ au point équivalent
$I = I_{0,1}' + I_{0,2} - I_{0,2}' + I_{0,2}'\,x$ après le point équivalent.

Puisque les différents coefficients $I_{0,1}$ représentent la densité du courant d'électrolyse observée sur une solution de chaque corps pris séparément à la concentration c_0, leur variation en fonction du potentiel de l'électrode est représentée par les courbes de polarisation de chacun de ces corps à la concentration c_0 (Fig. 4).

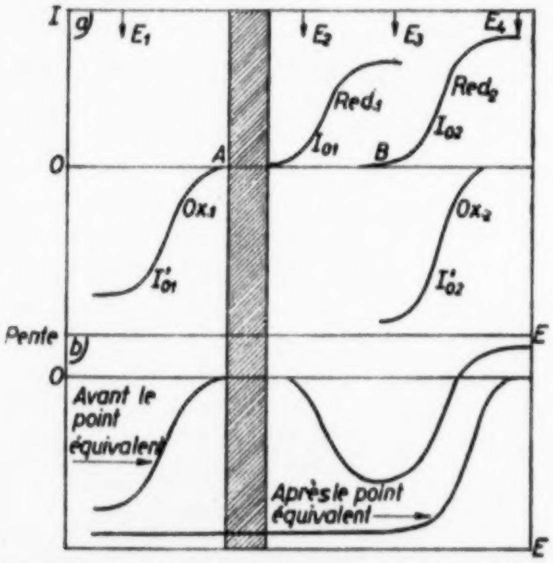

Fig. 4. a) Variation des paramètres I_0 en fonction du potentiel de l'électrode indicatrice.
b) Variations de la pente de la courbe avant et après le point équivalent. La zone hachurée indique le domaine de potentiel où le changement de pente au point équivalent est maximum.

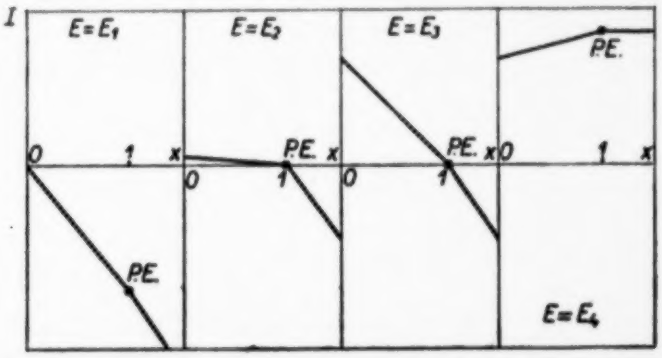

Fig. 5. Différentes formes de courbes ampérométriques. Les potentiels fixés correspondent à ceux de la Fig. 4.

La courbe de dosage est formée de deux droites qui se coupent au point équivalent. La figure 5 représente à titre d'exemple différentes courbes que l'on peut obtenir dans le cas du dosage d'un réducteur „irréversible" par un oxydant „réversible".

Contrairement à ce que l'on avait observé pour les réactions de précipitation,

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dans le cas des réactions d'oxydo-réduction, l'ordonnée au point équivalent peut être différente de zéro en l'absence de courant résiduel. Elle n'est nulle que si l'on fixe le potentiel à la valeur pour laquelle la courbe de polarisation d'un mélange de Ox_1 et de Red_2 à la concentration c_o coupe l'axe des abscisses ($I_{0,1}' + I_{0,2} = 0$).

En principe dans l'intervalle AB (Fig. 4), cette condition est réalisée. Mais pratiquement, pour différentes raisons, la courbe n'est pas confondue avec l'axe des abscisses et coupe celui-ci en un point, plus ou moins reproductible d'ailleurs. En prenant un potentiel autre que celui de ce point, on constate que la courbe de dosage $i = f(x)$ coupe l'axe des abscisses pour une valeur de x d'autant plus différente de 1 que la solution est plus diluée[5].

Remarquons enfin, que le potentiel que l'on doit fixer est celui que l'on mesure en potentiométrie statique ($i = 0$) au point équivalent.

Dans les autres cas le point équivalent ne peut être décelé que par un changement de pente qui doit être aussi net que possible.

Il est facile d'obtenir la courbe de variation de la pente de chaque droite en fonction du potentiel à partir des courbes de polarisation des corps Red_1, Ox_1, Red_2 et Ox_2 pris séparément à une concentration c_o (Fig. 4). On peut voir que c'est au voisinage du potentiel d'équilibre du système „irréversible" que la différence de pente est maximum, la première partie de la courbe ayant une pente sensiblement nulle et la deuxième partie ayant toujours une pente négative.

Les autres facteurs (excès d'électrolyte étranger, caractère quantitatif de la réaction, etc.) agissent sur les courbes de dosage comme dans le cas d'une réaction de précipitation.

DISPOSITIF EXPÉRIMENTAL

Circuit électrique. Reprenons le schéma général de la figure 6 avec

$$SI = \frac{V - E_A + E_C}{R + r}$$

Dans le cas de l'ampérométrie nous voulons que $E_A - E_C$ reste constant. I ne pouvant être infini, le numérateur du membre de droite doit tendre vers zéro en même temps que le dénominateur. Lorsque $R + r$ tend vers zéro $E_A - E_C$ tend vers V, c'est-à-dire une constante.

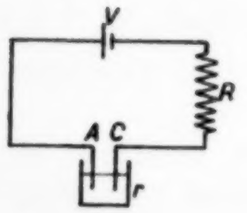

Fig. 6. Circuit électrique utilisé pour les dosages électrochimiques.

La constance de $E_A - E_C$ n'est pratiquement atteinte qu'avec une certaine approximation. Par exemple, pour une résistance totale de 1000 Ω, lorsque le courant varie de 0 à 10 μA, la tension appliquée varie déjà de 10 mv.

On n'a donc pas intérêt à utiliser de grandes intensités de courant. Par ailleurs, il est préférable de suivre l'intensité du courant limite de diffusion, (qui est le moins sensible aux variations de potentiel de l'électrode).

Remarquons enfin qu'aucune hypothèse n'a été faite sur la valeur de la tension V qui peut en particulier être nulle.

Electrode de référence. On utilise pour l'électrode de référence un système oxydo-

réducteur tel que son potentiel soit aussi indépendant que possible de l'intensité qui le traverse.

Supposons d'abord que nous formions une électrode de référence au moyen d'un fil de platine plongeant dans une solution d'un système oxydo-réducteur „réversible".

$$\text{Red} \rightleftarrows \text{Ox} + e$$

On peut écrire en première approximation l'équation de la courbe au voisinage du point où $I = 0$ et $E = E_0$ à partir de l'équation générale établie précédemment(1).

Lorsque $E \neq E_0$, on peut calculer

$$\frac{E—E_0}{I} \neq \frac{RT}{F}\left(1 + \frac{i_0}{I_d}\right)\left(1 - \frac{I_d}{I_d'}\right)\frac{1}{i_0} .$$

i_0 représente la valeur absolue commune à l'intensité du courant anodique partiel (oxydation de Red) et à celle du courant cathodique partiel (réduction de Ox) lorsque $E = E_0$: $i_A = -i_C = i_0$ (voir (1) page 178).

Lorsque le système devient plus „réversible", i_0 augmente, $E—E_0$ est moins sensible aux variations de I. Cependant, lorsque i_0 augmente indéfiniment, la sensibilité du potentiel aux variations de I ne tend pas vers zéro mais vers une valeur finie. A la limite on a

$$\frac{E—E_0}{I} \neq \frac{RT}{F}\left(\frac{1}{I_d} - \frac{1}{I_d'}\right) . \qquad (5)$$

Le terme entre parenthèses n'est jamais nul puisque I_d' est négatif.

Pour diminuer les variations de potentiel il faut:

1. prendre une électrode de grande surface; de cette façon pour une même intensité, la densité I et la variation de potentiel sont plus petites.
2. prendre des concentrations d'oxydant et de réducteur aussi grandes que possibles pour augmenter les densités I_d et I_d'.

En réalité on utilise des électrodes de référence du type $Hg/Hg_2Cl_2/KCl$. Le principe du fonctionnement est plus compliqué mais les conclusions pratiques restent valables.

Electrode indicatrice. Pour les potentiels élevés on utilise une électrode de platine tournante[6] ou vibrante[7]. Pour les potentiels négatifs on utilise l'électrode à gouttes de mercure, la courbe de polarisation des ions H^+ sur cathode de mercure étant fortement déplacée vers les potentiels négatifs.

On a intérêt en général à utiliser de très petites électrodes. L'intensité observée est suffisamment petite pour que la différence $E_A—E_C$ reste pratiquement constante comme nous venons de le voir, mais aussi la consommation de réactif par électrolyse est négligeable.

Par ailleurs la densité du courant résiduel ne semble pas dépendre beaucoup de la surface de l'électrode.

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Exemples d'application. L'ampérométrie à tension constante avec une seule électrode indicatrice connait actuellement un certain essor.

Elle a été appliquée à la précipitation de composés minéraux (phosphate d'uranium, cuivre ou zinc par le ferrocyanure, halogénures d'argent, chromate de plomb, sulfate de plomb, etc.) ou de composés organo-minéraux (cuivre-benzoïneoxime, nickel-diméthylglyoxime, argent-mercaptan, cadmium-naphtoquinoline, etc.).

Elle peut servir pour des réactions d'oxydo-réduction (Ti(III) par Fe(III), I_2 par $S_2O_3^{-2}$, V(II) par Fe(III), Cr(VI) ou V(V) par Fe(II)).

Enfin elle peut être utilisée au cours de réaction purement organiques telles que les réactions de copulation de sels de diazonium. On trouvera de nombreuses références dans Analytical Chemistry[8].

B. AMPÉROMÉTRIE AVEC DEUX ÉLECTRODES INDICATRICES "DEAD STOP END POINT"

Dans tous les cas que nous avons déjà étudiés, l'une des deux grandeurs E ou I était maintenue constante. Au contraire lorsqu'on maintient une différence de potentiel constante entre deux électrodes indicatrices, le potentiel de chacune d'elles et l'intensité varient.

La méthode décrite d'abord par FOULK ET BAWDEN[9] a déjà été expliquée qualitativement en particulier par DELAHAY[10]. FURMAN, REILLEY ET COOKE[11] ont introduit dans cette étude une équation de courbes de polarisation. Mais l'équation utilisée n'est valable que dans les cas de systèmes réversibles; par ailleurs ils limitent l'étendue de la méthode en n'utilisant que de petites tensions d'électrolyse et en attribuant un caractère différentiel à la courbe de dosage.

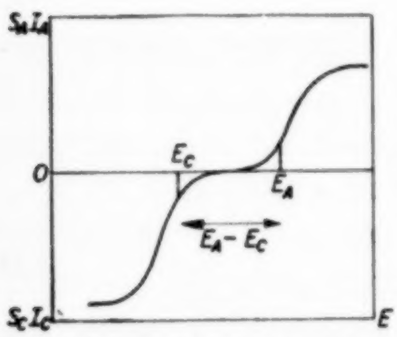

Fig. 7. Courbe de polarisation d'une solution à électrolyser

Relation entre l'intensité et la tension d'électrolyse. Les équations $i = f(E)$ utilisées précédemment donnent la relation entre l'intensité d'électrolyse et le potentiel de chacune des électrodes. Le problème est maintenant de calculer l'intensité d'électrolyse pour une différence de potentiel imposée entre les deux électrodes.

Considérons le cas simple où dans la solution existe un réducteur Red_1 et un oxydant Ox_2 ne réagissant pas chimiquement. En général les courbes de polarisation seront disposées comme sur la Fig. 7: la courbe de polarisation du mélange ne sera que la juxtaposition des courbes de polarisation individuelles ((1) page 178).

Si les deux corps sont suffisamment „irréversibles" pour l'intensité considérée on peut employer les équations simplifiées

$$E_A = E_{\frac{1}{2}} + \frac{RT}{\beta n F} \log \frac{I_A}{I_a - I_A} \qquad (6)$$

$$E_C = E_{\frac{1}{2}}' + \frac{RT}{\alpha' n' F} \log \frac{I_d' - I_C}{I_C} \qquad (7)$$

E_A est le potentiel de l'anode, E_C celui de la cathode, I_d et I_d' sont les densités de courant limite de diffusion du réducteur et de l'oxydant (la solution contenant un excès d'électrolyte indifférent), I_A et I_C sont les densités de courant anodique et cathodique. Dans les conditons d'électrolyse sous tension constante on a en outre

$$E_A - E_C = V \text{ (constante)} \qquad (8)$$
$$S_A I_A = -S_C I_C \qquad (9)$$

S_A et S_C étant les surfaces de l'anode et de la cathode.

La résolution des équations précédentes (en supposant pour simplifier $n = n' = 1$ et $\alpha = \beta = \frac{1}{2}$) permet d'établir la relation

$$\frac{-I_A^2}{\left(I_d - I_A\right)\left(\frac{S_C}{S_A} I_d' + I_A\right)} = e^{\frac{F}{2RT}\left[V - (E_{1/2} - E_{1/2}')\right]} = T \qquad (10)$$

Si Red_1 et Ox_2 appartiennent à des systèmes „réversibles" (en supposant toujours négligeables les concentrations des produits d'électrolyse), les coefficients α et β disparaissent des équations (6) et (7) et le terme T de l'équation (10) devient égal à

$$T = e^{\frac{F}{RT}\left[V - (E_{1/2} - E_{1/2}')\right]}$$

Si un seul des deux corps peut être considéré comme „réversible" un seul des coefficients α et β disparaît et l'équation (10) devient

$$\frac{I_A^3}{\left(I_d - I_A\right)\left(\frac{S_C}{S_A} I_d' + I_A\right)^2} = e^{\frac{F}{RT}\left[V - (E_{1/2} - E_{1/2}')\right]} \qquad (11)$$

ou

$$\frac{-I_A^3}{\left(I_d - I_A\right)^2\left(\frac{S_C}{S_A} I_d' + I_A\right)} = e^{\frac{F}{RT}\left[V - (E_{1/2} - E_{1/2}')\right]} \qquad (12)$$

selon que le réducteur ou l'oxydant est „réversible".

Si le réducteur et l'oxydant appartiennent au même système „irréversible", l'équation (10) s'applique, $E_{1/2}$ et $E_{1/2}'$ étant les potentiels de demi-vague anodique et cathodique. Si le système est „réversible" les équations (6) et (7) sont remplacées par

$$E_A = E_{1/2} + \frac{RT}{F} \log \frac{I_A - I_d'}{I_d - I_A} \tag{13}$$

$$E_C = E_{1/2} + \frac{RT}{F} \log \frac{I_C - I_d'}{I_d - I_C} \tag{14}$$

et l'équation (10) devient

$$\frac{\left(I_A - I_d'\right)\left(\frac{S_C}{S_A} I_d + I_A\right)}{\left(I_A - I_d\right)\left(I_A + \frac{S_C}{S_A} I_d'\right)} = e^{\frac{F}{RT} V} \tag{15}$$

elle est indépendante du potentiel $E_{1/2}$.

RÉACTION DE PRÉCIPITATION

Considérons encore la précipitation d'un réducteur Red. Pour que l'électrolyse puisse être réalisée la solution doit contenir un oxydant Ox_A("additional depolarizer"[10]).

Réaction de dosage. Comme précédemment nous écrivons la réaction

$$\text{Red} + A \rightleftarrows A\text{Red}\downarrow$$

la concentration de Red étant égale à c_0 (1-x) avant le point équivalent.

Réactions indicatrices. A l'anode, prédomine l'oxydation de Red et à la cathode la réduction de Ox_A :

$$\text{Red} - e \rightarrow \text{Ox}$$
$$\text{Ox}_A + e \rightarrow \text{Red}_A$$

Nous supposons que le courant reste suffisamment petit (pour que la quantité de Ox et de Red_A apparue reste négligeable) et que ces deux systèmes oxydo-réducteurs sont „irréversibles" pour les intensités envisagées.

Forme de la courbe de dosage. Dans ces conditions la densité du courant limite de diffusion de Ox_A, est constante. Celle de Red est donnée par l'équation

$$I_d = k_d F \,|\text{Red}| = k_d F c_0 (1 - x) = [I_d]_0 (1 - x) \tag{16}$$

$[I_d]_0$ étant la densité du courant limite de diffusion du réducteur titré dans les conditions initiales ($|\text{Red}| = c_0$).

En remplaçant I_d dans l'équation (10) par sa valeur en fonction de x on obtient l'équation de la courbe de dosage avant le point équivalent:

$$\frac{-I_A^2}{\left([I_d]_0(1-x) - I_A\right)\left(\frac{S_C}{S_A} I_d' + I_A\right)} = e^{\frac{F}{2RT}\left[V - (E_{1/2} - E_{1/2}')\right]} = T \tag{17}$$

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La courbe de dosage est un arc d'hyperbole (Fig. 8). Après le point équivalent, |Red| = 0 et l'intensité reste nulle en principe. Au point équivalent $I_A = 0$. Remarquons que l'équation précédente peut être mise sous la forme

$$I_A = [I_d]_\circ (1 - x) + \frac{I_A^2}{T \frac{S_C}{S_A} \left(I_d' + I_A \right)}$$

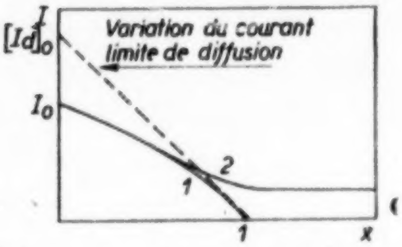

Fig. 8. Ampérométrie avec deux électrodes indicatrices.
Courbe 1: en l'absence de réducteur parasite
Courbe 2: action du réducteur parasite.

Le deuxième terme du membre de droite est négatif car $I_d' < 0$ et $\left| \frac{S_C}{S_A} I_d' \right| > I_A$. Vers le point équivalent, ce terme devient très petit (I_A tend vers zéro). I_A varie presque linéairement en fonction de x. Autrement dit la courbe admet comme tangente au point équivalent, la droite que l'on aurait obtenue en suivant la densité du courant limite de diffusion du corps titré. Elle s'en éloigne d'autant moins que l'on utilise une tension plus grande (T grand) et une anode plus petite, une cathode et une concentration d'oxydant plus grandes (I_d' grand).

Ces conditions sont illustrées par la figure 9. Pour une tension suffisamment grande, le point représentatif des conditions de fonctionnement de l'anode reste sur le palier de diffusion du corps titré (Fig. 9c).

Lorsqu'on diminue la surface de l'anode, l'intensité observable est plus petite. Le potentiel de la cathode et par suite celui de l'anode augmentent. Le point traduisant les conditions de fonctionnement de l'anode se rapproche donc du palier de diffusion du réducteur et peut même l'atteindre (Fig. 9b).

Lorsqu'on augmente la surface de la cathode ou la concentration de l'oxydant, la courbe de polarisation cathodique $S_C I_C = f(E)$ se trouve déplacée vers les

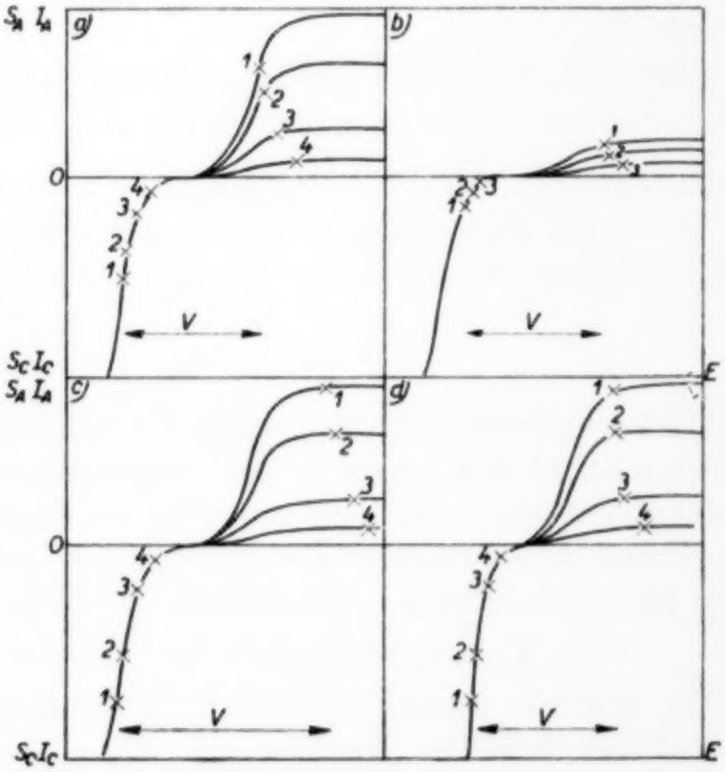

Fig. 9. Action des différents facteurs sur la courbe de dosage:
a) courbes de polarisation de référence pour $x = 0$; 0.3; 0.7; 0.9.
b) diminution de la surface anodique.
c) augmentation de V.
d) augmentation de la surface cathodique ou de la concentration de l'oxydant.

potentiels plus élevés, et on aboutit encore au même résultat (Fig. 9d).

Afin de se rendre compte quantitavivement de l'influence de ces divers facteurs, on peut calculer l'ordonnée de la courbe à l'origine (là où l'écart avec la droite limite est maximum):

$$I_\circ = [I_d]_\circ \frac{2is}{1 + is + \sqrt{(1\text{-}is)^2 + \frac{4is}{T}}} \qquad (18)$$

$$\text{où } i = -\frac{I_d'}{[I_d]_\circ}, s = \frac{S_C}{S_A}, T = e^{\frac{F}{2RT}[V-(E_{1/2}-E_{1/2}')]}$$

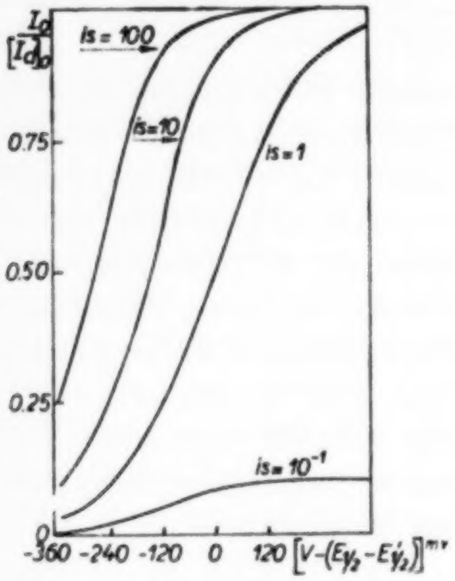

Fig. 10. Variation du rapport $\frac{I_o}{[I_d]_o}$ en fonction de la tension appliquée.

La figure 10 montre comment varie $I_\circ$ en fonction de $V-(E_{1/2}-E_{1/2}')$ pour différentes valeurs de *is*.

A partir d'un tel diagramme on peut trouver à priori les conditions pour que la courbe ne s'éloigne pas plus de 1 % par exemple de la droite limite.

Remarque: D'après certains auteurs, on observe avec la méthode de "dead stop end point" une brusque augmentation ou diminution du courant au point équivalent. En réalité, comme la partie de la courbe loin du point équivalent est souvent inutile dans les conditions employées jusqu'à présent, on utilise un galvanomètre très sensible. Il se produit une grande déviation dès qu'un petit courant apparaît. Mais cela suppose qu'il n'y a aucun des phénomènes parasites que nous envisageons maintenant.

Action d'un réducteur parasite. S'il existe un autre réducteur que le corps titré, la densité de courant n'est jamais rigoureusement nulle. En l'absence du corps titré et par conséquent à partir du point équivalent, à une tension appliquée V correspond une densité de courant constante I_p.

On peut démontrer qu'il subsiste un point anguleux plus ou moins net au point équivalent (Fig. 8).

Contrairement à ce que nous avions observé en utilisant une électrode de référence, la courbe de dosage avant le point équivalent ne subit pas une simple translation d'amplitude I_p. Le potentiel de l'anode croît au cours du dosage et l'action du réducteur parasite augmente. Les courbes observées en présence et en l'absence du réducteur parasite se séparent d'autant plus tôt, que les courbes de polarisation des deux corps sont plus rapprochées.

On peut encore démontrer que lorsque la tension V, le rapport $\frac{S_A}{S_C}$ ou I_d' augmentent, la pente de la courbe immédiatement avant le point équivalent devient plus négative et tend de nouveau vers $-[I_d]_\circ$. Ces conditions correspondent au maximum de netteté du point équivalent. Cependant la fraction de la

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densité de courant due au réducteur parasite peut devenir très grande (si la densité de son courant limite de diffusion est grande); la variation relative du courant entre le point initial et le point équivalent devient plus petite. La précision expérimentale intervient alors pour limiter la précision de la détermination du point équivalent.

Réaction non rigoureusement quantitative. Pratiquement les réactions ne sont pas rigoureusement quantitatives. La variation de |Red| n'est linéaire — comme nous l'avons supposé — qu'en première approximation. En réalité, au point équivalent il reste une concentration de réducteur d'autant plus grande que la réaction est moins quantitative. Il en résulte une disparition du point anguleux.

Alors qu'en ampérométrie avec électrode de référence, le point équivalent pouvait être déterminé par extrapolation des parties rectilignes de la courbe, on ne peut utiliser cet artifice dans le cas présent, que si la tension utilisée est suffisamment grande pour que la partie de courbe située avant le point équivalent soit pratiquement rectiligne. Cela suppose alors qu'aucun réducteur n'intervient encore pour la tension appliquée, comme nous venons de le voir.

AUTRES TYPES DE PRÉCIPITATION

1. D'une manière générale l'équation (10) (ou ses analogues) peut se mettre sous la forme

$$I = I_d - f(I)$$

ou $f(I)$ est une fonction croissante de I à une puissance supérieure à 1. Au point équivalent où I est petit la tangente sera toujours la droite $I = I_d$. On peut ainsi prévoir à titre d'exemple pour une réaction rigoureusement quantitative les courbes de la figure 11 lorsque le corps titrant seul ou lorsque les deux réactifs sont électroactifs. Dans ce dernier cas la portion de courbe qui se sépare le plus vite de sa tangente au point équivalent correspond au réducteur le moins énergique.

Les différents facteurs agissent comme dans le cas précédent. En particulier la présence d'un réducteur parasite rend l'angle des deux tangentes, au point

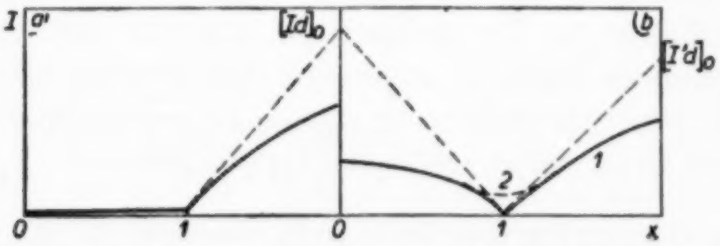

Fig. 11. Réaction de précipitation. Courbes ampérométriques obtenues avec deux électrodes indicatrices.
Courbe (a): le corps titrant est seul électroactif.
Courbe (b)1: les deux corps sont électroactifs.
Courbe (b)2: action d'un réducteur parasite.

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équivalent plus obtus (Fig. 11) et si la réaction est insuffisamment quantitative, ce point auguleux disparaît.

Le cas des oxydants serait traité d'une manière identique.

2. Nous avons supposé que l'oxydant auxiliaire avait sa courbe de polarisation située de telle façon (Fig. 7) que la courbe de polarisation du mélange pouvait être considérée comme la simple superposition des courbes de polarisation de l'oxydant et du réducteur.

Remarquons alors que l'on peut prendre comme oxydant auxiliaire l'antagoniste du réducteur titré. Si le système Red/Ox est „irréversible" on est ramené au cas précédent.

3. Si le système est „réversible", on utilise de la même façon l'équation (15), en remplaçant I_d par sa valeur; on en déduit l'équation de la courbe de dosage. On obtient une courbe semblable à celle de la figure 8. Cependant la tangente au point équivalent de la première portion de courbe à une pente variable, inférieure en valeur absolue à $[I_d]_0$. Elle ne tend vers $[I_d]_0$ qu'en augmentant V, s et i. Les mêmes facteurs agissent d'ailleurs pour appliquer la portion de courbe sur sa tangente au point équivalent (Fig. 12).

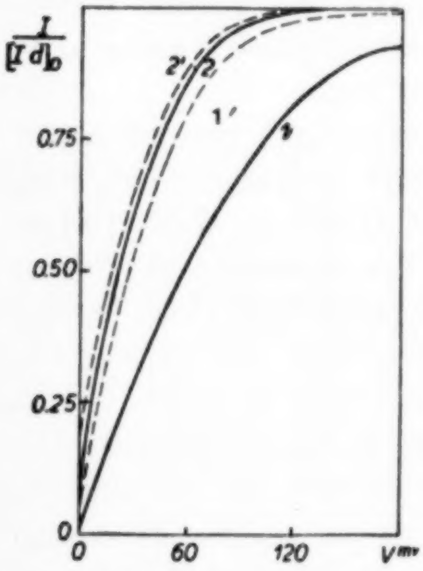

Fig. 12. Réaction de précipitation d'un réducteur en présence de l'oxydant antagoniste. Courbes 1 et 2: ordonnée à l'origine de la courbe de dosage pour $i = s = 1$ et $i = s = 10$. Courbes 1' et 2': ordonnée à l'origine de la tangente au point équivalent des courbes précédentes.

On remarquera, que dans ce cas c'est V seul et non $[V-(E_{1/2}-E_{1/2}')]$ qui intervient; pratiquement on pourra donc utiliser des tensions beaucoup plus petites. La figure montre également que la courbe devient vite confondue pratiquement avec sa tangente lorsque i et s augmentent. Le calcul montre d'ailleurs que les facteurs déterminants sont maintenant is et $i + s$ et que l'on a intérêt à prendre i et s du même ordre de grandeur lorsqu'on cherche à augmenter le produit is.

Si la courbe de réduction de l'oxydant auxiliaire Ox_A est située à droite de la courbe d'oxydation du réducteur, on observe souvent une réaction plus ou moins lente entre les corps, aussi n'avons nous pas envisagé ce cas.

RÉACTIONS D'OXYDO-REDUCTION

La méthode a surtout été employée dans ce cas.

Réaction de dosage. Nous supposerons que l'on titre un réducteur par un oxydant selon

$$\mathrm{Red}_1 + \mathrm{Ox}_2 \rightleftarrows \mathrm{Ox}_1 + \mathrm{Red}_2$$

Les concentrations varient comme nous l'avons indiqué page 70.

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Réactions indicatrices. En principe à l'anode prédominent les deux oxydations

$\mathrm{Red_1} - e \rightarrow \mathrm{Ox_1}$
ou $\mathrm{Red_2} - e \rightarrow \mathrm{Ox_2}$
et à la cathode $\mathrm{Ox_1} + e \rightarrow \mathrm{Red_1}$
ou $\mathrm{Ox_2} + e \rightarrow \mathrm{Red_2}$

Forme de la courbe de dosage. Supposons que les deux systèmes oxydo-réducteurs soient „irréversibles" comme le représente la Fig. 13a. Lorsqu'ils sont mélangés dans des conditions correspondant au dosage avant le point équivalent, on voit (Fig. 13b) que la courbe de polarisation individuelle de $\mathrm{Ox_2}$ n'existe pas $|\mathrm{Ox_2}| = 0$).

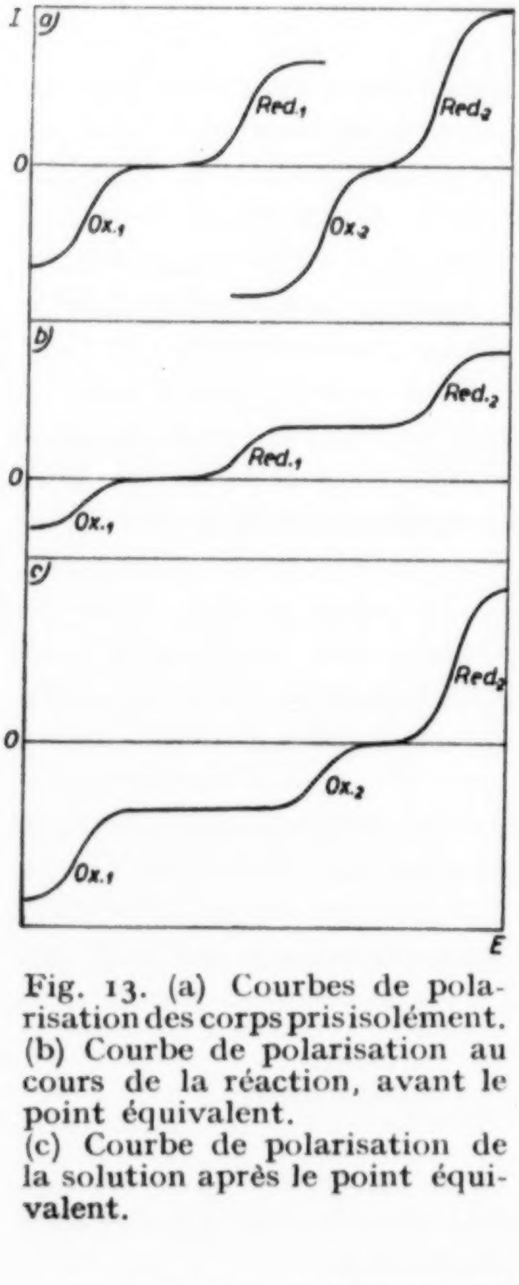

Fig. 13. (a) Courbes de polarisation des corps pris isolément.
(b) Courbe de polarisation au cours de la réaction, avant le point équivalent.
(c) Courbe de polarisation de la solution après le point équivalent.

La courbe de polarisation de $\mathrm{Red_2}$, se trouve à droite de celle de $\mathrm{Red_1}$; autrement dit, dans un assez grand domaine de potentiel l'intensité du courant d'oxydation de $\mathrm{Red_2}$ est négligeable vis-à-vis de celle de $\mathrm{Red_1}$. Donc pratiquement, tant que l'on n'impose pas une tension d'électrolyse trop grande, tout se passe comme si le système $\mathrm{Ox_1/Red_1}$ était seul.

La figure 13c montre que parallèlement, après le point équivalent, le système $\mathrm{Ox_2/Red_2}$ fixe pratiquement seul, l'intensité d'électrolyse. On peut ainsi utiliser les équations précédemment établies. Avant le point équivalent, l'équation (10) où l'on fait

$$I_d = [I_{d1}]_\circ (1-x) \text{ et } I_d' = [I_d{}'_1]_\circ\, x$$

représente l'équation de la courbe de dosage avant le point équivalent. $[I_{d1}]_\circ$ et $[I_{d1}']_\circ$ sont respectivement les densités des courants limites de diffusion de $\mathrm{Red_1}$ et de $\mathrm{Ox_1}$ à la concentration initiale $c_\circ$.

La courbe est encore une portion d'hyperbole. Pour préciser sa forme on peut calculer les tangentes à l'origine et au point équivalent, où I_A est nul.

Au voisinage de l'origine l'équation de la courbe peut se mettre sous la forme

$$I_A = -\frac{S_C}{S_A} I_d' - \frac{I_A^2}{T_1(I_d - I_A)} \neq -\frac{S_C}{S_A}[I_{d_1}']_\circ x - \frac{I_A^2}{T_1[I_{d1}]_\circ}$$

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et au voisinage du point équivalent

$$I_A = I_{d1} + \frac{I_A^2}{\left(\frac{S_C}{S_A} I_{d1}' + I_A\right) T_1} \neq [I_{d1}] (1-x) + \frac{I_A^2}{T_1 \frac{S_C}{S_A} [I_{d1}']_0}$$

Les seconds termes des membres de droite deviennent négligeables lorsque I_A tend vers zéro. Ainsi, au voisinage du point équivalent la courbe de variation de la densité du courant anodique admet comme tangente la droite que l'on aurait obtenue en suivant le courant limite de diffusion du réducteur qui disparaît. A l'origine c'est au contraire le courant limite de diffusion de l'oxydant qui apparait qui fixe la pente de la droite (avec un facteur $\frac{S_C}{S_A}$ puisque la limitation se produit du côté cathodique alors que nous raisonnons sur la densité anodique) (Fig. 14).

L'hyperbole à son maximum sur la droite AB, et la densité est égale à

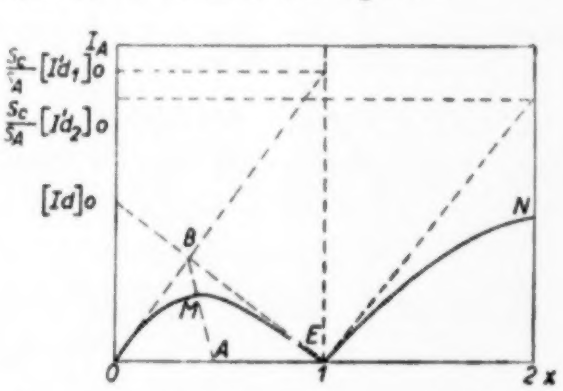

Fig. 14. Courbe ampérométrique d'une réaction d'oxydo-réduction, suivie avec deux électrodes indicatrices.

$$I_M = [I_{d1}]_0 \frac{si \sqrt{T_1}}{\sqrt{T_1} (1 + si) + 2 \sqrt{si}} \tag{19}$$

avec

$$s = \frac{S_C}{S_A}, \; i = - \frac{[I_{d1}']_0}{[I_{d1}]_0} \text{ et}$$

$$T_1 = e^{\frac{F}{2RT}[V-(E_{1/2,1}-E_{1/2,1}')]}$$

Le terme i est maintenant une constante caractéristique du système Red_1/Ox_1.

Au-delà du point équivalent la même équation (10) est utilisable en faisant

$$I_d = [I_{d2}]_0 \text{ et } I_d' = [I_{d2}']_0 (x-1).$$

On obtient encore un arc d'hyperbole. L'équation mise sous la forme

$$I = -\frac{S_C}{S_A} [I'_{d2}]_0 - (x-1) - \frac{I_A^2}{T_2([I_{d2}]_0 - I_A)}$$

montre que la courbe ampérométrique obtenue en suivant l'intensité du courant limite de diffusion de l'oxydant Ox_2 sert de tangente à la courbe précédente pour $x = 1$, (avec le facteur $\frac{S_C}{S_A}$, pour la raison déjà exposée).

Pour $x = 2$, on peut calculer l'intensité observée au moyen de l'équation (18) dans laquelle

$$s = \frac{S_C}{S_A},\ i = \frac{[I_{d2}']_\circ}{[I_{d2}]_\circ} \text{ et } T = T_2 = e^{\frac{RT}{2F}[V - (E_{1/_2,2} - E_{1/_2,2}')]}$$

Action des différents facteurs sur la forme de la courbe

1. L'augmentation du paramètre T augmente les intensités I_M en I_N que l'on peut utiliser comme repères.

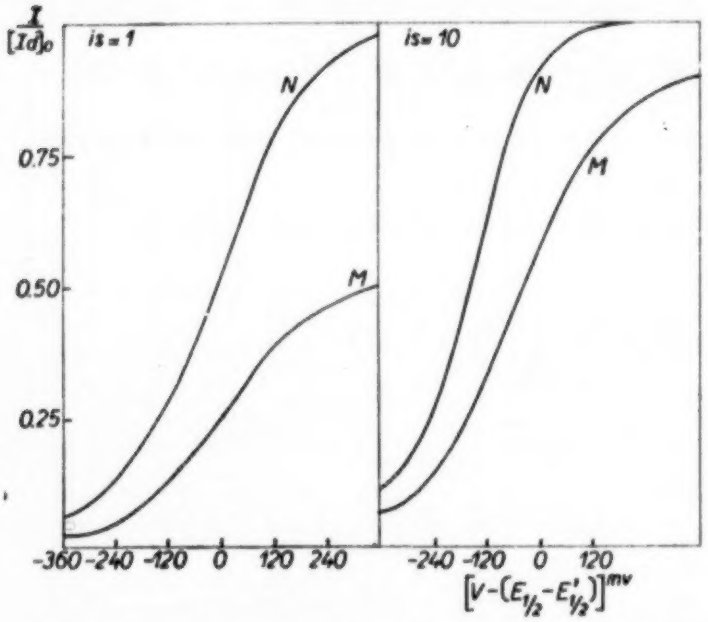

Fig. 15. Les courbes M donnent le rapport $\frac{I}{(I_{d1})_\circ}$ au point M.

Les courbes N donnent le rapport $\frac{I}{(I_{d2})_\circ}$ au point N.

L'augmentation de T, peut être obtenue en accroissant la tension d'électrolyse (Fig. 15). Si elle est trop petite, le courant n'est plus décelable. Par ailleurs, pour une même tension d'électrolyse V, moins un système est ,,irréversible'' plus les potentiels des demi-vagues anodiques et cathodiques sont rapprochés et plus le paramètre T est grand. Ainsi pour chacun des deux systèmes, l'intensité est d'autant plus élevée qu'ils sont plus réversibles. Autrement dit, sur la Figure 15, les courbes M et N sont translatées horizontalement l'une par rapport à l'autre d'une quantité égale à $(E_{1/_2,1}-E_{1/_2,1}')-(E_{1/_2,2}-E_{1/_2,2}')$. On peut prévoir alors des formes de courbes analogues à celles de la Figure 16. Si aucun système parasite n'intervient, en augmentant suffisamment la tension appliquée on doit toujours finir par observer une courbe analogue à la courbe (a).

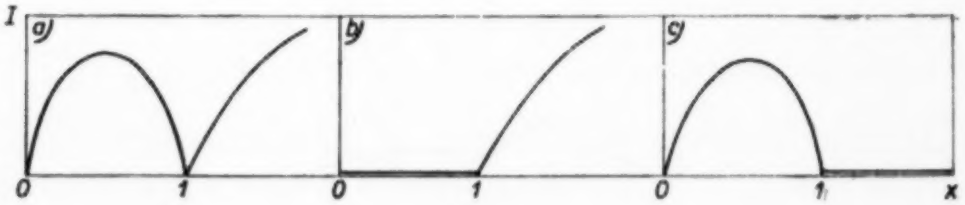

Fig. 16. Courbes ampérométriques obtenues au cours d'une réaction d'oxydo-réduction, avec deux électrodes indicatrices:
(a) deux systèmes de même réversibilité ($E_{1/_2}$—$E_{1/_2}'$ voisin pour les deux systèmes).
(b) le système titrant est le plus réversible.
(c) le système titré est le plus réversible.

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Le rapport $\frac{[I_d']_\circ}{[I_d]_\circ}$ est imposé par la nature du système oxydo-réducteur. Le rapport $\frac{S_C}{S_A}$ doit maintenant être fixé au voisinage de l'unité. Lorsque ce rapport augmente par exemple, la portion de courbe BE (Fig. 14) se rapproche de sa tangente alors que la protion EN s'en éloigne plus rapidement et le point équivalent n'est pas décelé avec plus de précision.

2. En réalité au point équivalent même pour une réaction rigoureusement quantitative, le courant n'est pas rigoureusement nul. Au voisinage de ce point, Red_2 joue vis-à-vis de Red_1 le même rôle que le réducteur parasite dans la précipitation de Red; la courbe subit une déformation analogue.

Cette déformation sera d'autant plus importante que les courbes de polarisation de Red_2 et de Red_1 seront plus voisines.

Cette déformation peut encore être produite par un réducteur parasite dont la courbe de polarisation est située entre celle de Red_1 et celle de Red_2.

La même chose est observée du côté des oxydants sur la portion de courbe située après le point équivalent.

Cas des systèmes réversibles. L'application de l'équation valable à la limite lorsqu'un système est suffisamment „réversible" ($E_{1/2} \neq E_{1/2}'$ permet de prévoir des courbes de dosage analogues aux courbes (a) ou (c) de la figure 16. Comme dans le cas de la précipitation, la pente de la tangente à l'origine et au point équivalent ne reste pas constante, elle augmente avec la tension appliquée et tend vers la pente observée avec les systèmes „irréversibles". Simultanément la courbe se rapproche de ces tangentes.

DISPOSITIF EXPÉRIMENTAL

Le circuit électrique est le même que celui de l'ampérométrie classique, mais l'électrode de référence est remplacée par une deuxième électrode indicatrice.

EXEMPLES D'APPLICATIONS

La précipitation d'un oxydant en présence d'un réducteur auxiliaire a été utilisée pour doser les chlorures par l'argent, le réducteur auxiliaire était NO_2 [12].

La précipitation d'un réducteur en présence de l'oxydant antagoniste a été réalisée sous la forme de la précipitation du ferrocyanure de zinc en présence de ferricyanure (d'après DELAHAY[10]).

En oxydo-réduction on a surtout utilisé le dosage de l'iode par le thiosulfate sous différentes formes[9, 13].

La Figure 17 représente la courbe obtenue au cours du dosage de V(V) par Fe(II) d'après GALE ET MOSHER[14]. La tension appliquée était suffisante pour que le système V(V)/V(IV) puisse réagir aux deux électrodes, mais à ce moment le système Fe(II)/Fe(III) plus réversible donne après le point équivalent, une

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courbe qui reste très près de sa tangente au point équivalent. Fe(III) jouant le rôle de système parasite vis-à-vis de V(V) donne un point d'inflexion avant le point équivalent (comparez à la figure 11).

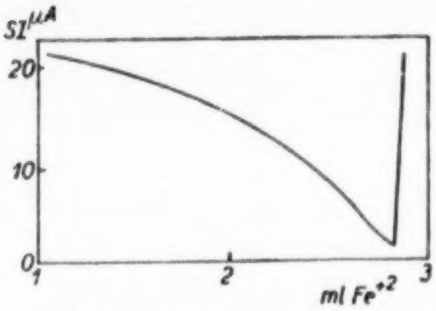

Fig. 17. Ampérométrie avec deux électrodes indicatrices. Dosage de V(V) par le Fe(II) (d'après GALE ET MOSHER).

La méthode a également été appliquée au dosage de Fe(III) par l'acide ascorbique[15].

Le dosage de l'iodure par le brome est un exemple de réactions d'oxydo-réduction entre deux systèmes réversibles, KIES[16] a étudié ce dosage et comparé les polarogrammes tracés à différents stades de la réaction.

Enfin, en cours de rédaction, nous avons eu connaissance de l'étude expérimentale du dosage de Fe(II), $[Fe(CN)_6]^{-4}$, Ti(III) par Ce(IV) ou MnO_4^-, V(V) par Fe(II) et Fe(III) par Ti(III)[17].

COMPARAISON DES MÉTHODES AMPÉROMÉTRIQUES ET POTENTIOMÉTRIQUES

L'ampérométrie sous tension constante avec deux électrodes indicatrices a l'avantage de la simplicité du montage. On évite l'utilisation d'une électrode de référence et du pont électrolytique la reliant à la solution dosée.

Par contre elle a l'inconvénient de donner une courbe de dosage sur laquelle le point équivalent ne peut plus être décelé quand la réaction n'est pas très quantitative — à moins que l'on puisse utiliser une tension suffisante sans être gêné par les oxydants ou les réducteurs parasites.

L'ampérométrie avec électrode de référence n'a pas cet inconvénient, puisqu'en général une réaction quantitative seulement à 10 % près donne une courbe de dosage qui par extrapolation des parties rectilignes permet de déceler encore le point équivalent avec une précision de 1 %. Cependant pour garder cet avantage l'ampérométrie classique nécessite des conditions assez strictes pour la constance de la tension appliquée, et la résistance du circuit extérieur. En outre, lorsqu'on utilise l'électrode de platine on observe parfois une instabilité des intensités mesurées ou bien la loi $i = kc$ est mal suivie de sorte que l'extrapolation devient de nouveau impossible.

Il semble que de ce point de vue, la potentiométrie à intensité constante soit préférable. L'intensité du courant n'a pas besoin d'être proportionnelle à la concentration, une légère variation des conditions expérimentales, a peu d'influence. Les conditions sont moins rigoureuses (par exemple l'intensité imposée peut varier de 10 %).

Enfin lorsque la réaction devient moins quantitative, la précision ne diminue pas plus vite en potentiométrie à intensité constante qu'en ampérométrie classique.

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GÉNÉRALISATION DE L'AMPÉROMÉTRIE ET DE LA POTENTIOMÉTRIE

La potentiométrie à intensité constante et l'ampérométrie à tension constante avec ou sans électrode de référence ne sont que des cas limites d'une méthode plus générale, que l'on pourrait appeler potentiométrie ou ampérométrie à résistance constante[18]. En effet si nous considérons le schéma électrique de la figure 6, l'intensité $S_A I_A$ qui traverse le circuit, les potentiels de chaque électrode et les concentrations du réducteur et de l'oxydant (en ne considérant que le réducteur le plus énergique et l'oxydant le plus énergique) sont reliés par les équations suivantes

$$\frac{V - E_A + E_C}{R + r} = S_A I_A \ , \ I_A = f_1\,(E_A, |\mathrm{Ox}|, |\mathrm{Red}|)$$

$$\text{et} \quad - I_C = f_2\,(E_C, |\mathrm{Ox}|, |\mathrm{Red}|), \ S_A I_A = - S_C I_C$$

Les fonctions f_1 et f_2 traduisent l'équation de la courbe de polarisation de la solution. La forme des courbes de dosage dépend alors uniquement des paramètres V, et $R + r$. Dans le cas général, il revient au même de mesurer $E_A - E_C$ (potentiométrie) ou I_A (ampérométrie) puisque $E_A E_C = V - I_A S_A\ (R + r)$ les deux grandeurs sont des fonctions linéaires l'une de l'autre. L'étude de la forme des courbes est très compliquée, les potentiels E_A et E_C intervenant en puissances et en exponentielles variées.

Lorsqu'on utilise une électrode de référence (fonctionnant comme cathode par exemple) on peut écrire

$$E_A = V + E_C - S_A I_A (R + r) \text{ ou } I_A = \frac{V + E_C}{S_A(R + r)} - \frac{E_A}{S_A(R + r)}$$

Cette équation représente une droite dans le système d'axes $I_A = f(E)$, dont les points d'intersection avec le réseau de courbes de polarisation tracées pour différentes valeurs de x, donnent les ordonnées correspondantes de la courbe de dosage (potentiométrique ou ampérométrique). L'équation de cette courbe malgré l'élimination de E_C reste encore très compliquée (E_A intervenant encore en puissances et en exponentielles).

On simplifie encore lorsque la droite devient pratiquement horizontale ou pratiquement verticale.

Dans le premier cas, $R + r$ est très grand. Si V n'est pas lui-même très grand, I_A est très petit et on est pratiquement dans les conditions de la potentiométrie classique.

Si V est grand, I_A est notable mais est pratiquement constant. La variation de I_A n'est pas nulle, mais elle est difficilement décelable; au contraire la variation de E_A qui est égale à $R + r$ fois celle de I_A est facilement mesurable et on effectue de préférence la potentiométrie à intensité constante.

Dans le deuxième cas $R + r$ est très petit, V pouvant être nul ou non I_A varie

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beaucoup alors que E_A varie peu. La variation de I_A est la plus facilement mesurable, on effectue donc de préférence une ampérométrie.

Lorsque les deux électrodes sont indicatrices on peut seulement écrire

$$S_A I_A = \frac{V}{R+r} - \frac{(E_A - E_C)}{R+r}$$

Si V est nul E_A—E_C et I_A sont nuls. Si V est suffisamment grand, I_A reste pratiquement constant et par conséquent chaque électrode fonctionne indépendamment l'une de l'autre. Comme précédemment seule la potentiométrie est réalisable.

Si $R + r$ est très petit, E_A—E_C est pratiquement constant, alors que I_A varie beaucoup, on effectue donc de préférence l'ampérométrie ("dead stop"). E_A et E_C varient simultanément, les deux électrodes ne sont pas indépendantes.

Ces courbes — aussi bien ampérométriques que potentiométriques d'après ce que nous venons de dire — sont formées de deux droites lorsque $R + r$ est petit puis elles deviennent logarithmiques lorsque $R + r$ augmente.

L'influence de la résistance R a été étudiée expérimentalement par GOFFART, MICHEL ET PITANCE[19] dans le cas de l'oxydation de Mn(II) par Mn(VII) ou Ce(IV) en présence d'acide pyrophosphorique.

RÉSUMÉ

Les courbes de polarisation, dont les propriétés ont été étudiées dans un article précédent, permettent de préciser les meilleures conditions de dosage par ampérométrie à tension constante avec ou sans électrode de référence (dead-stop end-point). En particulier, on peut ainsi établir quantitativement les conditions d'emploi de cette dernière méthode.

Par ailleurs, la relation générale qui existe entre les méthodes potentiométriques et ampérométriques a été mise en évidence et ces différentes méthodes comparées.

SUMMARY

Polarisation curves, the properties of which have been studied in a previous article, permit accurate definition of the best conditions for amperometric determination at constant voltage with or without a reference electrode (dead-stop end-point). In particular, the conditions for this latter method can be established quantitatively.

On the other hand, the general relation which exists between potentiometric and amperometric methods has been demonstrated, and these different methods compared.

ZUSAMMENFASSUNG

Mit Hilfe der Polarisationskurven, deren Eigenschaften in einer früheren Veröffentlichung beschrieben worden sind, kann man die besten Bedingungen für die amperometrische Bestimmung bei konstanter Spannung mit oder ohne Vergleichselektrode (dead-stop end-point) festlegen. Insbesondere kann man so die Anwendungsbedingungen der letzteren Methode quantitativ ermitteln.

Anderseits wurde das allgemeine Verhältnis zwischen den potentiometrischen und amperometrischen Methoden hervorgehoben und diese verschiedenen Methoden verglichen.

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NACHWEIS VON AMINOSÄUREN, ASCORBINSÄURE UND ZUCKERN MIT ALKALIKOBALTIKARBONAT UND CHROMISALZEN

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Vom dreiwertigen Kobalt kennt man ausser den Kobaltiaken verschiedene Komplexverbindungen, von denen die Alkalicobaltikarbonate $Me_3[Co^{III}(CO_3)_3]$ noch wenig untersucht sind[1]. Es sind dunkelgrüne, in Wasser leicht lösliche Verbindungen, die bei neutraler oder schwach alkalischer Reaktion sehr beständig sind. Man kann ihre wässerige Lösung kürzere Zeit zum Sieden erhitzen, ohne dass sie Zersetzung erleiden. Der Karbonatrest lässt sich durch die verschiedensten Radikale leicht ersetzen, so dass man hier eine Methode besitzt, die gestattet bequem zu andern Komplexen zu gelangen. Die wässerige Lösung lässt sich leicht herstellen durch Lösen von Alkalibikarbonat in Wasser, Versetzen mit Wasserstoffsuperoxyd und allmähliches Zufügen von Kobaltosalz, wobei sich momentan die dunkelgrün gefärbten Alkalikobaltikarbonate bilden. Für die vorliegenden Versuche wurden 7 g Kaliumbikarbonat in 50 ml Wasser gelöst, mit 10 ml 3%igem Wasserstoffperoxyd versetzt und eine konzentrierte Lösung mit 2.4 g Kobaltochlorid langsam unter Umrühren zugefügt, wobei sich stürmisch Kohlendioxyd entwickelt und das überschüssige Wasserstoffperoxyd durch das Kobalt zersetzt wird.

Das Kobalt bildet andrerseits mit dem Aminosäuren äusserst stabile Komplexe in Form von Chelaten $[Co(H_2N\text{-}R\text{-}COOH)_3]$, die sich selbst in konzentrierter Schwefelsäure unzersetzt lösen. Sie existieren in zwei stereoisomeren Formen und besitzen tief violette Farbe. Für ihre Darstellung wird angegeben, man solle frisch gefälltes Kobaltihydroxyd mit den betreffenden Aminosäuren kochen[2]. Viel bequemer erfolgt die Darstellung jedoch durch Erwärmen der entsprechenden Aminosäure mit einer Lösung von Alkalikobaltikarbonat. Nach kurzem Sieden werden die grünen Lösungen vorübergehend blau, indem sich wahrscheinlich Aquokomplexe bilden und es entweicht Kohlendioxyd. Bei weiterem Erhitzen während ca ½ Minute nehmen die Lösungen die charakteristische violette Farbe der Aminosäurekobaltiake an. Diese Reaktion ist charakteristisch für die Aminosäuren. Beim vorsichtigen Schichten auf konzentrierte Schwefelsäure bleibt im

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TABELLE I

REAKTIONEN DER AMINOSÄUREN MIT KALIUMKOBALTIKARBONAT

	Reaktion beim Erwärmen	Reaktion mit Schwefelsäure	Löslichkeit *iso*Butylalkoh.	Löslichkeit Äthyllaktat
Glykokoll	violett	violett	—	—
α-Alanin	lila	blaulila	—	partiell
β-Alanin	blau	rosaviolett	—	
Serin	rotviolett	violett	—	—
Cystin	braunviolett braunes CoS	hellrosa Co^{II}	—	—
Threonin	lila	violett	—	—
Methionin	violett	braun	+	+
Phenylalanin	violett	violett	+	+
Tyrosin	rosa	braunrosa	+	+
Tryptophan	violett, trüb	tieforange	+	+
Dijodtyrosin	braunrosa	braunrosa Fällung	+	+
Histidin	blau, dann rot	rosaviolett	—	partiell
Valin	violett	violett	+	+
Norvalin	violett	violett	+	+
Leucin	violett	violett	+	+
Arginin	blaulila	hellviolett	—	—
Ornithin	blaulila	violett	—	partiell
Lysin	blaulila	violett	partiell	partiell
Asparaginsre	violett	violett	—	—
Glutaminsäure	blaulila	violett	—	—
Prolin	blauviolett	lila	partiell	+
Oxyprolin	blaulila	rosaviolett ausbleichend	Spur	Spur
Asparagin	rotviolett	violett	—	—
Histamin	blaulila	farblos	—	partiell
Betain	grün	hellrosa Co^{II}	—	—
Sarkosin	lila	rosaviolett	—	partiell
Glycylglycin	rotviolett	rosakarmin	—	Spuren
Kreatinin	olivbraun	farblos Co^{II}	—	—
Kreatin	grün	farblos		
Glykocyamin	grün	farblos		

allgemeinen die violette Farbe erhalten, während bei andern Kobaltiaken ein Umschlag nach schwach rosa erfolgt. Proteine geben keine solche Reaktionen, beim Kochen entsteht eine hellgraubraune Fällung. Aceton, Formaldehyd, Acetaldehyd und Harnstoff werden nicht verändert, Zitrate reduzieren in der Wärme langsam zu rötlichen Kobaltoverbindungen. Die Zucker geben mit Ausnahme der Saccharose einen lila gefärbten Niederschlag, der sich mit viel Kaliumkarbonat lila löst und mit Natronlauge eine tiefblaue Lösung ergibt. Die Sacharose ist offenbar nicht im Stande das dreiwertige Kobalt zu reduzieren und die Lösung bleibt grün. Ascorbinsäure reduziert schon in der Kälte zu einer rosa gefärbten Kobalt-2-Verbindung. Harnsäure gibt beim Kochen einen graulila

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gefärbten Niederschlag. Die Nachweisgrenze für Glykokoll liegt bei 100 γ/ml, für Tryptophan bei 200 γ/ml und für die gelbe Fluorescenz bei 0.2 γ/ml.

Verschiedene Aminosäurekobaltiake lassen sich mit *iso*Butanol, oder noch besser mit Äthyllaktat nach Sättigung der wässerigen Phase mit Natriumsulfat

TABELLE II

REAKTIONEN VON AMINEN UND ZUCKERN MIT KALIUMKOBALTIKARBONAT

	Reaktion beim Erwärmen	Reaktion mit Schwefelsäure	Löslichkeit in *iso*Butanol	Löslichkeit in Äthyllaktate
Harnstoff	grün	rosa	—	—
Harnsäure	graulila Fällung	rosa		
Formamid, Propion-Butyr-, Valeramid	grün	rosa		
Cholin	braune Fällung	rosa		
Piperidin	grün	rosa	—	grün
Pyrrol	grün	rosa	—	—
Pyridin	blaulila	hellrosa	+	+
Putrescin	blau	grün	partiell	partiell
Äthylendiamin	karminrosa	rosa	eosinrot	eosinrot
Ammoniak	rotviolet, in Kälte blau	rosa	—	—
Anilin	hellrosa	dunkeloliv		
Methylamin	blaulila	rosa	—	—
Nicotinsäureamid	grün	rosa		
Adenin, Vit. B_6	lilabraune Fällung	hellgelblich		
Pyridoxamin	orangeoliv blaue Fluoresc.	gelbe Fluoresc.		
Colamin	braunlila Niederschlag	violett	—	partiell
Hippursäure	braune Fällung	rosa		
Guanidin	schwarzgrüne Fällung	rosa		
Uracil	grün	rosa		
Antifebrin	grüne Fällung	hellrosa		
p-Aminobenzoesäure	braune Fällung	braun		
Casein	graubraune F.	gelb,	—	—
Eieralbumin	graubraune F.	gelb, grüne Fluoresc.	—	—
Pepton	graubraune F.	rosa	—	—
Arabinose, Glykose, Galaktose, Laktose, Maltose	hellila Fällung, in NaOH tief blau	hellrosa	—	—
Rohrzucker	grün	hellrosa	—	—
Glukosamin	braune Fällung	rosa, dann braun	—	—
Aceton	langsam rosa	hellrosa	—	—

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ausschütteln, namentlich solche mit grossem organischen Rest, wie Phenylalanin, Tyrosin und Tryptophan. Auch mit Kaliumkarbonat lassen sich die Kobaltiake in die Esterschicht treiben, manchmal nur bis zu einem gewissen Prozentsatz, ausgenommen natürlich saure Aminosäuren, wie die Glutaminsäure. Bei solchen Fällen wurde in den Tabellen I und II die Bezeichnung partiell eingetragen. Das Zeichen + bedeutet, dass der Komplex quantitativ in die Esterschicht übergeht nach Sättigung mit Kaliumkarbonat oder Natriumsulfat.

Wie man sieht gibt das Betain mit dem dreifach methylierten Stickstoffatom keine Reaktion mit dem Reagens. Sehr empfindlich ist die Reaktion des Tryptophankobalts mit konzentrierter Schwefelsäure. Wenn man Tryptophan allein in Schwefelsäure löst, so entsteht eine hellgelbe Lösung mit gelber Fluorescenz im UV, die auf Zusatz von Alkali nach bläulichweiss umschlägt. Der Tryptophankobaltikomplex löst sich dagegen tief orangegelb mit gelbgrüner Fluorescenz. Mit Lauge schlägt die Farbe der Fluorescenz nach ultramarinblau um. Die verschiedene Extrahierbarkeit der Aminosäurekobaltiake mit *iso*Butanol oder Äthyllaktat kann man zur Trennung der Aminosäuren benutzen.

Es wurde versucht die Aminosäuren in Urin nachzuweisen. Gibt man zu 5 ml Urin 1 ml Äthyllaktat und sättigt mit Kaliumkarbonat, so scheidet sich der gelbe Harnfarbstoff, das Urochrom, mit dem Ester als ölige Schicht ab. Wenn man nun die wässerige Schicht mit Kaliumkobaltikarbonat erwärmt, so erhält man rötlichviolette Lösung infolge Reduktion des Kobalts und die Esterschicht färbt sich höchstens schwach gelb. Setzt man zum Urin etwas Alanin und Histidin so färbt er sich beim Erwärmen violett und die Esterschicht nimmt die Komplexe mit violetter Farbe auf, und die Farbe bleibt beim vorsichtigen Aufgiessen auf konzentrierte Schwefelsäure bestehen.

Versuche mit Vanadintrichlorid gaben beim Erwärmen mit Natriumacetat und Methionin oder Lysin grüne Lösungen. Die grüne Verbindung liess sich mit Äthyllaktat und Natriumsulfat extrahieren. Es zeigte sich aber, dass bereits Oxydation zu vierwertigem Vanadin eingetreten war, denn eine Lösung von blauem Vanadylchlorid mit vierwertigem Vanadin gab mit Natriumacetat und einer Aminosäure erwärmt, ebenfalls grüne Verbindungen, die sich mit Äthyllaktat nach Sättigung mit Natriumsulfat extrahieren liessen. Etwas stabiler sind Titanochloridlösungen. Diese werden nach Zugabe von Natriumacetat bräunlich und werden beim Erwärmen mit Tryptophan oder Tyrosin tiefbraun. Wenn man Äthyllaktat zufügt und mit Natriumsulfat sättigt, so gehen nur Spuren der braunen Verbindungen in die Esterschicht über.

Da das Chrom ähnliche Komplexe wie das Kobalt liefert, wurde versucht mit Chromihexaquochlorid und mit Chloropentaquochromichlorid die Innerkomplexe mit Aminosäuren darzustellen. Wenn man solche Lösungen mit Natriumacetat abpuffert und mit einer Aminosäure erwärmt, so schlägt die tiefgrüne Farbe nach rotviolett um. Ammoniak gibt eine grüne Fällung, die sich beim Erhitzen bläulichgraugrün verfärbt. Die Komplexe sind gegen Säuren empfindlicher, als die entsprechenden Kobaltsalze, lössen sich aber allgemein etwas leichter in *iso*Butylalkohol oder in Äthyllaktat nach Sättigung der wässerigen Phase mit Natriumsulfat. Gewisse Vorteile bietet die Verwendung von Hexureachromichlorid $[Cr(OC(NH_2)_2]_6Cl_3$. Es wird von Phosphat und Karbonat nicht gefällt, was bei der Untersuchung von Urin von Vorteil ist, Ammoniak führt es in rosa gefärbte Chromiake über.

Das Triglycylchrom $[Cr(H_2NCH_2COO)_3]$ lässt sich mit Äthyllaktat höchstens spurenweise extrahieren, die Verbindung mit Alanin aber bereits fast vollständig. Das Cystin gibt wie alle übrigen Aminosäuren mit Chrom ebenfalls einen rotvioletten Komplex, während das Kobalt eine braune Fällung von Sulfid liefert. Der Cystin-chromkomplex ist in Äthyllaktat löslich. Beim Erwärmen mit Casein oder Harnsäure entstehen graublaugrünliche Niederschläge und mit Kreatin tritt keine Reaktion ein. Auch Zucker sind ohne Einwirkung auf das Reagens.

Es wurde versucht im Urin eines Knaben, der an Aminosäureurie litt, die Aminosäuren nachzuweisen. 6 ml Urin wurden mit Natriumsulfat gesättigt und dreimal mit 2 ml Äthyllaktat ausgeschüttelt, um das Urochrom zu entfernen. Nach Zugabe einer Messerspitze Hexureachromichlorid und Natriumacetat und einigen Tropfen Essigsäure wurde aufgekocht und extrahiert. Die Esterschicht besass eine rötliche Farbe. Mit dieser Reaktion kann man auch den Abbau von Proteinen durch Fermente kontrollieren. Nach der Verdauung einer Fibrinflocke mit Pepsin in 0.2 %iger Salzsäure liessen sich nur wenig Aminosäuren mit Äthyllaktat als Chromkomplexe nachweisen, sehr deutlich aber nach Verdauung mit Pankreatin bei pH 7.5. Eine Fibrinflocke wurde in 5 ml Wasser gebracht, mit einer Messerspitze Pankreatin versetzt und das pH mit Natriumkarbonat auf 7.5 eingestellt. Nach 30 Minuten wurde 1 ml entnommen, mit wenig Hexureachromichlorid und Natriumacetat erwärmt und extrahiert. Die Lösung blieb aber grün. Nach drei Stunden wurde bereits eine rotviolette Lösung erhalten, der sich aber nur wenig Komplexe mit Äthyllaktat entziehen liess. Nach zwölfstündiger Einwirkung des Ferments wurde beim Erwärmen mit Hexureachromichlorid eine tiefviolette Lösung erhalten, der sich der grösste Teil der Chromiaminosäurekomplexe durch Äthyllaktat extrahieren liess. Der Abbau zu den einfachen Aminosäuren war also ziemlich vollständig.

ZUSAMMENFASSUNG

Durch Einwirkung von grünem Kaliumkobaltikarbonat oder von Aquochromichlorid, oder Hexureachromichlorid auf Aminosäuren in wässeriger Lösung erhält man die violettgefärbten Innerkomplexe der Aminosäuren mit Kobalt und Chrom, die sich zum Teil mit *iso*Butanol oder mit Äthyllaktat nach Sättigung der wässerigen Phase mit Natriumsulfat exthahieren lassen. In konzentrierter Schwefelsäure lösen sich die meisten Kobaltkomplexe unzersetzt mit violetter Farbe, während die Chromverbindungen grün werden.

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SUMMARY

By the action of potassium cobalticarbonate, aquochromic chloride, or hexaureachromic chloride on amino acids, in aqueous solution, violet complexes of amino acids with cobalt and chromium are obtained. They can be extracted and separated with *iso*butanol or ethyl lactate, after the saturation of the aqueous phase by sodium sulphate. Most of the cobalt complexes dissolve without decomposing in concentrated sulphuric acid, giving a violet coloration, while the chromium derivatives give a green coloration.

RÉSUMÉ

Par action du cobalticarbonate de potassium, ou du chlorure d'aquochrome, ou encore du chlorure de chrome hexaurée sur les acides aminés, en solution aqueuse, on obtient des complexes internes violets: acides aminés — cobalt et acides aminés — chrome. Ils peuvent être extraits en partie avec l'*iso*butanol ou avec le lactate d'éthyle, après saturation de la phase aqueuse par le sulfate de sodium. La plupart des complexes cobaltiques se dissolvent sans décomposition dans l'acide sulfurique concentré, en donnant une coloration violette, tandis que les dérivés du chrome donnent une coloration verte.

LITERATUR

[1] FIELD UND QUART, *J. Chem. Soc.*, 14 (1862) 51; G. A. BARBIERI, *Atti Accad. Lincei*, [6] 7 (1928) 747; C. DUVAL, *Compt. rend.*, 191 (1930) 615.
[2] H. LEY UND H. WINKLER, *Ber.*, 42 (1909) 3894; 44 (1911) 3279.

Eingegangen den 20. November 1952

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Ordinary Meeting of the Society

An Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, December 3rd, 1952, in the Meeting Room of the Chemical Society, Burlington House, Piccadilly, London W. 1. Dr. J. R. NICHOLLS, President of the Society, was in the Chair, and a Lecture on *Industrial Fluorosis* was given by H. H. GREEN, O.B.E., D. Sc., and was illustrated by a film, lantern slides and exhibits.

Synopsis of Lecture

The significance of emission of fluorine compounds into the atmosphere by industrial undertakings in relation to the health of man and animals, and in relation to damage to vegetation, was discussed, with particular reference to agricultural and social implications in relation to industrial interests.

At least 28 industrial occupations of man have been associated with fluorine hazards, but many of these are within towns and do not concern farm stock unless the factories are in the vicinity of farm land on to which particulate matter can be carried by wind and deposited on pastures. Of the large industries affecting local agriculture those discussed included aluminium production, brick-works, enamel or colour factories, the iron and steel industry, and collieries.

Analytical techniques for fluorine in various materials were referred to, together with methods for assessing fluorine hazards and the need for further research into control measures.

Ordinary Meeting of the Scottish Section

An Ordinary Meeting of the Scottish Section was held at 7.15 p.m. on Thursday, December 11th, 1952, in the Biochemistry Department, The University, Glasgow, W. 2, when a Lecture on *Electrophoresis* was given by Dr. G. T. MILLS (Department of Biochemistry, University of Glasgow).

Mr. H. C. MOIR was in the Chair and sixteen members and friends were present.

The lecture was followed by a visit to the Electrophoresis Laboratory, where apparatus and equipment for the determination of moving boundary, optical method, and zonal electrophoresis on filter paper was inspected and discussed.

Synopsis of Lecture

The technique of electrophoresis is the study of the migration of charged particles in solution under the influence of an applied potential. The introduction of the TISELIUS optical method for the study of boundary electrophoresis in 1937 opened up new fields of study, which have been further expanded by the introduction of zone electrophoresis on filter paper. The lecture covered the main theoretical and practical features of these methods.

Physical Methods Group

The *Eighth Annual General Meeting* of the Physical Methods Group of the Society of Public Analysts and Other Analytical Chemists was held at 6 p.m. on Tuesday, November 25th, 1952, in the Meeting Room of the Chemical Society, Burlington House, Piccadilly, London W.1.

Dr. J. HASLAM occupied the Chair and there were 41 other members present.

The Annual General Meeting was followed at 6.30 p.m. by the *Thirty-Eighth Ordinary Meeting* of the Group. The Chair was taken by Dr. J. **Haslam** and about 62 members and visitors were present.

The following papers on *Forensic Science* were presented and discussed:

The Application of Some Physical Methods in Forensic Science with Particular Reference to the Examination of Materials Relating to Criminal Investigation, by J. B. **Firth**, D.Sc., F.R.I.C., M.I.Chem.E.

The investigator is continually meeting problems of identification of miscellaneous specimens. Among these are fragments of glass and precious stones for which density, hardness and refractive index all play an important part.

Certain solids are recognised by melting-point, and liquids, e.g., mixed petroleum products, by fractional distillation or boiling-point determination. Ultra-violet fluorescence is employed for the examination of stones, while spectrographic analysis is an invaluable tool for the identification of minute specimens of paint, glass, etc. Carbon monoxide can be estimated by spectral absorption in the visible region, and certain alkaloids by their ultra-violet absorption. Other methods involve colorimetry or nephelometry or chromatographic examination. In most cases several methods may be applied to one microscopic specimen to gain as much information as possible.

The Examination of Questioned Documents, by J. A. C. **McClelland**, B. Sc., Ph.D., A.R.I.C.

Examination of documents which may have been mishandled in any way such as to convey an impression different from that originally intended is carried out. This involves such processes as the reproduction of erased writing, the detection and presentation of added or altered particulars or of markings which have been faintly imprinted on documents. Other articles which may bear obliterated or altered impressions may also require examination.

The presence of materials foreign to the article under examination may also give valuable information as to the nature of any mistreatment which may have taken place.

The methods employed for this work involve the use of various type of illumination which are obtained by means of light filters or special types of lamps. Thus for working in the infra-red region, a suitable filter and photographic plate is used whilst the appropriate colour filter is needed for the reproduction of marks on a coloured object. For working in the ultra-violet region a suitable lamp is employed.

The examination of typescript will usually reveal characteristics which should enable the identification of a certain machine; when this is possible any documents typed on one specific instrument can usually be considered to emanate from the same source.

Any evidence which may be obtained as a result of these investigations is reproduced in a manner suitable for presentation as evidence in a court of law.

Biennial Dinner

The Society will hold its Biennial Dinner (79th Anniversary) at the *Hall of the Worshipful Society of Apothecaries of London*, Blackfriars Lane, London, E.C.4, on Friday, March 6th, 1953.

Reception at 7 p.m. Dinner at 7.30 p.m. Evening dress, with decorations, will be worn.

The President, Dr. J. R. **Nicholls**, C.B.E., F.R.I.C., will be in the Chair, and a number of distinguished guests will be present. On this occasion the Society's Medal will be presented to the first two Bernard Dyer Memorial Lecturers, Sir E. John **Russell** and the Honourable Mr. Justice Lloyd **Jacob**.

The price of the Tickets will be £2 5s., inclusive of aperitifs and wine and of waiters' gratuities.

A vegetarian or other special meal can be served if desired, if members will notify me.

The Council trusts that this will be the occasion of a representative gathering of members of the Society, and that the President will have the support of your presence, with any guests you may wish to bring. Ladies are welcomed.

Please notify the Secretary of your intention to be present, and of the names of your guests, as soon as possible, as accommodation is very strictly limited.

Yours faithfully,
K. A. WILLIAMS,
Honorary Secretary.

BOOK REVIEW

Anorganisches Grundpraktikum für Chemiker und Studierende der Naturwissenschafte, by CARL MAHR. Verlag Chemie, G.m.b.H., Weinheim/Bergstrasse, 1952, XV and 332 pages, 53 fig., 16 microphoto's. DM 15.—

For such readers as are not quite well-posted on German University customs the title of this book may be slightly misleading. In accordance with its title it gives indeed a set of exercises in simple inorganic syntheses, but at the same time it is a complete laboratory manual of inorganic qualitative analysis for young students, and as such in many respects quite a success.

It shows that in Germany the conviction is now gradually gaining ground that it is desirable and possible to incorporate modern methods and modern techniques into preliminary courses of qualitative analysis, without abandoning the didactical values of the old conceptions. In a commendable way it calls attention to the use of organic reagents, to microscopic reactions and to micro and semi-micro techniques in general. It goes without saying that the author's selection of microscopic identity reactions and of spot-tests is rather arbitrary. Each worker in this field has his own favourites and his own black sheep; that is inevitable and rather an advantage as it often enables us to get out of an old groove. Anyhow the set of identity reactions recommended here seems to be well thought-out and deserving a fair trial.

Now that the first step has been successfully taken one may express the hope that in the course of time the author will come to the conviction that the old-fashioned macro-analytical part of his book might just as well have been left out altogether. To my mind it must be considered as nothing but a concession to conservatism.

C. J. VAN NIEUWENBURG (Delft)

VOL. 8 (1953) ANALYTICA CHIMICA ACTA

THE SENSITIVITY OF ANALYTICAL REACTIONS AND THE SELECTIVITY OF SOME NEW ORGANIC REAGENTS

by

J. GILLIS *

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INTRODUCTION

The purpose of this paper is to illustrate the work done in the Laboratory of Analytical Chemistry of the University of Ghent in Belgium, in connection with the "Committee on Analytical Reactions" of the I.U.P.A.C. It has been related to the definition and graphical representation of the sensitivity of analytical tests and to the search for new organic reagents and the improvement of certain types of organic compounds containing characteristic groupings for inorganic ions.

SENSITIVITY OF ANALYTICAL TESTS

1. The general problem

A mixture to be analysed includes the following substances:

1° Constituent A, the amount of which is *a*;
2° Solvent B, the amount of which is *b*;
3° Constituent C, the amount of which is *c*. Constituent C represents the extraneous substances altogether.

The general problem will be the determination or the detection of constituent A, in presence of the extraneous substances C, when A+C are dissolved in solvent B.

2. Mixtures of $A + B + C$

All possible mixtures of A, B and C, in amounts *a*, *b* and *c* can be represented graphically in a system of rectangular coordinates, if cologarithmic functions

$$pA = -\log a \qquad pB = -\log b \qquad pC = -\log c$$

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* Paper presented at the Symposium on Analytical Chemistry held at Birmingham on September 11th and 12th by the Midlands Society for Analytical Chemistry.

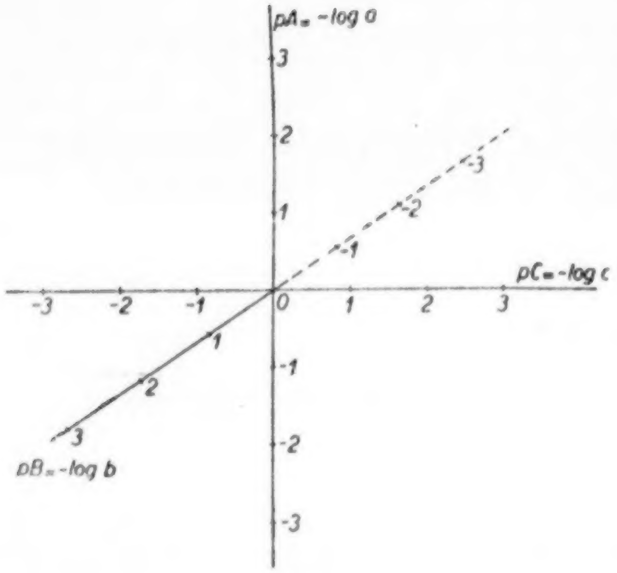

Fig. 1

are placed on the three axes, as in Fig. 1.

Each point of this system will correspond to a given mixture, the origin of the system being a mixture containing A, B and C in unit amounts.

3. *Diagram pA, pC at constant pB*

If the amount of solvent B remains constant, a section through the spatial figure, where pB = — log b = constant, leads to a diagram in which each point represents a mixture of A + C dissolved in a constant quantity of solvent B. If this quantity is chosen equal to unity, pB will become zero and Fig. 2 is obtained.

On this diagram are now superimposed the curves which are the geometric locus of mixtures of A and C, having a constant sum: $a + c$. Such curves are designated in Fig. 2, for instance by $a + c = 10^{-1}, 10^{-2}, 10^{-3}$, and so on. Each point of these curves can represent the composition of a sample, weighing 10^{-1}, 10^{-2}, 10^{-3} grams for instance, dissolved in an amount of solvent $b = 1$. These curves can be called *sample-lines of constant weight.*

Each point of the diagram corresponds to a definite ratio $a / (a + c)$ and also belongs to a line parallel to the first bisector, whose distance to this line is a function of the ratio a/c or c/a, because, by means of logarithms:

$$\text{pA} - \text{pC} = -\log a/c = \log c/a.$$

In the same way we can obtain the ratio a/b, making the difference between pA and pB, thus:

$$\text{pA} - \text{pB} = -\log a/b = \log b/a.$$

Diagrams of this kind: pA, pC for pB = constant are of interest in analytical chemistry and in many other spheres. They give the relative amounts of each

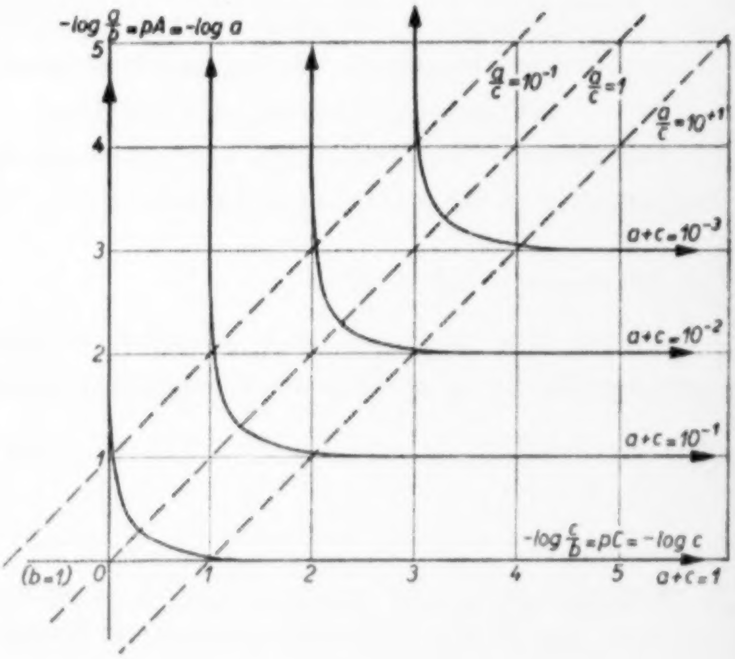

Fig. 2

constituent as well as the percentage and the concrete amounts in each mixture, and, with a supplementary, they can correlate definite properties such as solubility, conductivity, potential, etc. with the exact composition of mixtures of two components A and C, dissolved in a constant quantity of solvent B. For dilute solutions and trace analysis, for instance, they are far superior to the classical diagrams relating percentage to a given physico-chemical property.

4. *Diagram pA, pB at constant pC*

The same conditions hold for mixtures of constituent A with variable amounts of solvent B, but with constant amounts of extraneous substance C. Fig. 3 gives the corresponding diagram. It is only necessary that pC remains constant; if c = 0, pC = — infinity, a supposition for which Fig. 3 is also applicable. The system is only binary in that case; we have now to detect or to determine substance A in a solvent B, in the absence of extraneous substances.

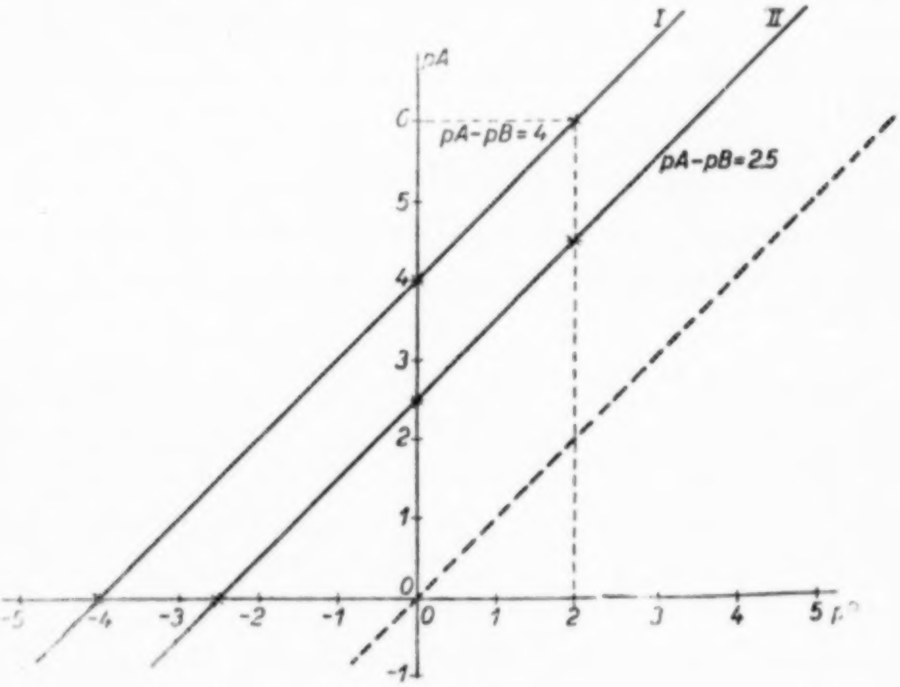

Fig. 3

Each point of the diagram is situated at a definite distance of the first bisector and we have, for a line parallel to this bisector:

$$\text{pA} - \text{pB} = -\log a/b = \text{constant}$$

If pA — pB is positive, this line is situated above the first bisector and the ratio a/b is smaller than unity. This will always be the case in analytical chemistry and in trace analysis, where the amount a of constituent to be detected or determined in a mixture is lower than the amount b in which it is dissolved.

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If the ratio a/b has reached the value for which the detection of A in B is barely positive by means of a given test, the line parallel to the first bisector going through the corresponding point will be the limit between two areas, the mixtures above the line will give a negative test, while the mixtures situated under this line will give a positive test. This line is *the sensitivity-line of the test* in question.

Suppose line I of Fig. 3 to be the sensitivity-line of a given test, the *concrete* amounts used, at the limit of sensitivity, being $a = 10^{-6}$ and $b = 10^{-2}$. This line is situated above the first bisector, going through pA = 6 and pB = 2. The difference pA — pB = 4 corresponds to a ratio $a/b = 10^{-4}$.

Two other points on this line are especially significant: the first, with the coordinates pA = 4 and pB = 0, can be called the *limit of concentration*, giving the amount a of constituent A detectable in one unit of solvent ($b = 1$); the second, corresponding to coordinates pA = 0 and pB = — 4, can be called *limit of dilution*, giving the amount of solvent in which one unit of constituent A ($a = 1$) may be detected. The ratios a/b and b/a have reciprocal values, as given by the identity:

$$a/b = 1 : b/a.$$

The first ratio gives the "concentration" of the solution, the second the "dilution".

This identity is the key to the well-known relation, introduced by FEIGL[1] in 1923:

$$\frac{\text{Identification limit (in } \mu\text{g)}}{\text{Volume of sol. (in ml)} \cdot 10^6} = 1 : \frac{\text{Vol. of sol. (in ml)} \cdot 10^6}{\text{Identification limit (in } \mu\text{g)}}$$

The notation, introduced by FEIGL at the same time, as an expression of the sensitivity of a given test, can be written: $a\,[T]^b$, a being the identification limit (in µg) and b the volume of solvent (in ml), the letter T recalling the analytical technique used (spot plate, filter paper and so on).

FEIGL characterised the sensitivity of a given test by the *concrete* values of a (*effective* identification limit) and of b (*effective* volume used). In Fig. 3, this corresponds, for instance for line I, with the point pA = 6 and pB = 2. To homogenise the units used: micrograms for a and millilitre for b, a factor 10^6 must be introduced. This factor is necessary *on both sides* of the expression given above, where the first member corresponds with the point pA = 4 and pB = 0 (the *limit of concentration*), while the denominator b/a of the second member corresponds with the point pA = 0 and pB = — 4 (the *limit of dilution*).

WENGER[2], in the editorial of the "Second Report", used the same expression, namely $1 : \dfrac{b \cdot 10^6}{a}$, but called it limit of dilution, although it equals the limit of concentration. If a and b are measured in the same unit (for instance in

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micrograms), the expression of the sensitivity of the "Second Report" becomes:

$$D = 1 : \frac{b}{a} = \frac{a}{b} = 10^{-n}$$

Wenger introduced indeed the use of negative exponents of the basis 10, as a uniform convention, to simplify the script.

Taking the negative logarithms of the last expression, we have:

$$-\log D = +n = -\log a - (-\log b)$$

or

$$\mathrm{pD} = +n = \mathrm{pA} - \mathrm{pB}$$

if pD = — log D and pA = — log a and pB = — log b.

This means that, using cologarithms, the sensitivity of a test can be given by a positive number $+ n$, the distance between the first bisector on Fig. 3 and the sensitivity-line of the test[3].

The proposal to characterise the sensitivity of a definite test by means of a positive number was accepted by the "Committee on Analytical Reactions" in its last meeting held in New York in 1951.

For this conventional definition of the sensitivity, see also[4].

5. *Sensitivity diagram*

In order to describe quantitatively the influence of definite amounts of interfering substances on the sensitivity of an analytical test, I have made use, since 1945, of diagrams pA, pC at pB = 0. I called the figures thus obtained "sensitiv-

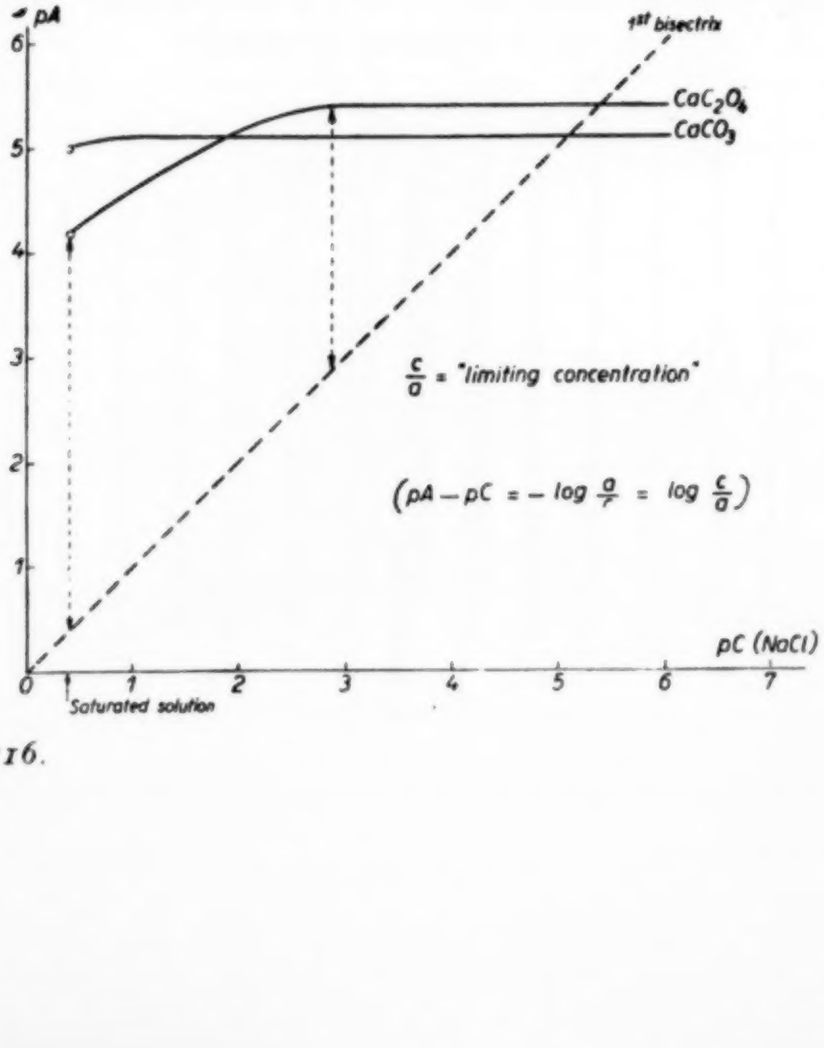


Fig. 4

ity diagrams" and in 1950, in Graz, I described in detail the construction and practical use of them[5].

A simple example is given by Fig. 4, where NaCl, in solutions more concentrated than 1 per cent., lowers the sensitivity of the well-known reaction of Ca with NH_4-oxalate, but is without effect on the reaction using NH_4-carbonate. In detecting a particular "impurity" (here Ca) in a given commercial substance (here NaCl), the test of $CaCO_3$ is more sensitive than the classical test of $Na_2C_2O_4$. This example shows how sensitivity-diagrams can be useful in comparing different tests for the same element in the presence of increasing amounts of attendant material.

Another advantage of the sensitivity-diagram is that it gives the ratio c/a at the point where the sensitivity of the test begins to be affected. This ratio is given by the difference $pA - pC = \log c/a$, or by the distance between the point considered and the first bisector. This ratio corresponds with the notion of ***limiting concentration***, called „Grenzverhältnis" by SCHOORL in his microchemical researches, published in 1907.

In the same manner the last point of the curve, corresponding with the saturation of the interfering substance, can be considered and the limiting concentration c/a, in saturated solution, can be deduced. This ratio may be of interest in the detection of an "impurity" or a trace in the strongest possible solution of a commercial substance.

A *sensitivity-diagram* describes all the quantitative aspects of one or of different tests in the presence of attendant substance. Knowing pA, pB and pC, it is possible to know: the effective identification limit pA; the effective volume or weight of the solvent used in the test, namely pB; the sensitivity $pA - pB = + n$; the limiting concentrations $pA - pC$, corresponding with the different concentrations $pC - pB$ of the interfering substance.

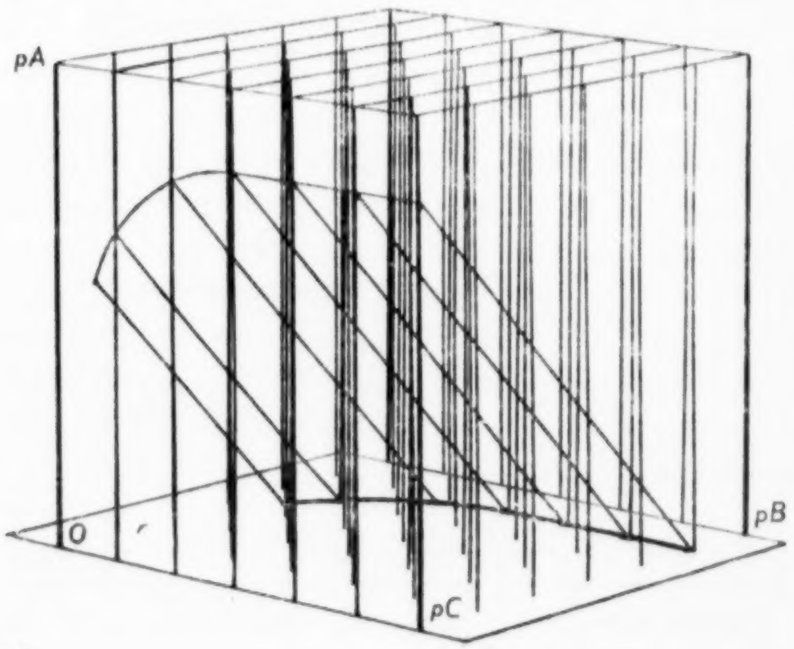


Fig. 5

At a glance one can see, on the sensitivity-diagram, if the reaction is affected (curve going downward or upward), or not, by the attendant substance.

6. *The spatial figure pA, — pB, pC*

The complete spatial figure (Fig. 5) gives the correlation of the diagrams described in Figs. 3 and 4.

On the front of the three-dimensional diagram pA, — pB, pC it is easy to observe a ***sensitivity-diagram*** : pA, pB = 0, pC, analogous to Fig. 4.

On the right, one can see a section pA, — pB, pC = 6, analogous to Fig. 3. The ***sensitivity-line*** is passing by — pB = 5 and pA = 5. When pC becomes smaller (it is when the amount *c* becomes higher) all the sensitivity-lines are forming a plane, cutting the front and tracing the downwards curved line of the ***concentration limits*** pA — pB = — log *a*/*b*, for different values of pC, and cutting the bottom of the special figure, tracing a heavy line giving the corresponding ***dilution limits*** of the same test under the same conditions.

Semiquantitative analysis

It is possible to evaluate approximately the amount of constituent in a mixture A + B + C, by diluting it in known proportions until a definite analytical test becomes negative.

The principle of the method can be easily understood by means of a sensitivity-diagram of the given test (see Fig. 6).

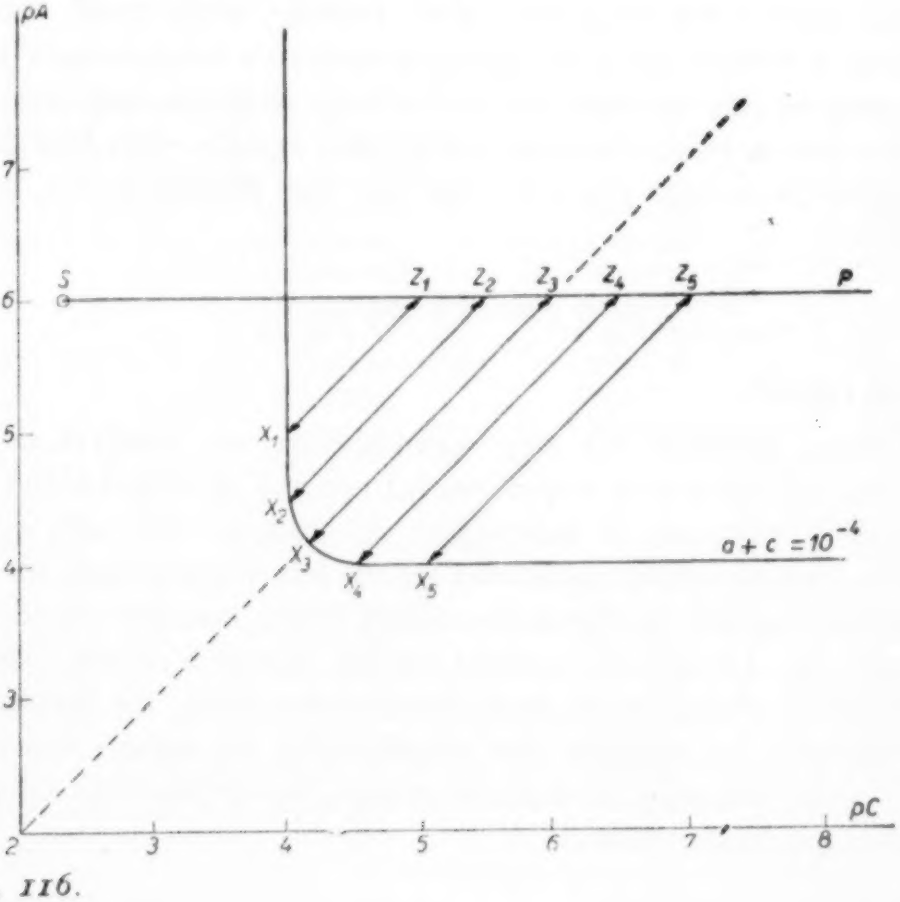


Fig. 6

Suppose the amount of copper to be estimated roughly in brass. A will represent Cu and C the non-copper in the brass to be analysed. We dissolve 0.1 g of sample and bring the volume of the solvent B to 1000 ml. Mixtures of A + C having all possible percentages of copper are to be found on the line $a + c = 10^{-4}$, the richest copper-mixtures on the right-hand side, the poorest on the left and upwards.

Using cuproine as reagent for copper, a reagent virtually specific for copper and fairly sensitive without interferences, we have, for a given technique, pA — pB = 6. The line of the concentration limits SP will remain horizontal until the saturation of C, in solvent B, is reached.

By adding water to the initial solution, the ratio a/c remains constant, but the ratio a/b becomes smaller and smaller. The point representing the unknown will move, on dilution, along a line parallel to the first bisector, until the line SP is reached.

The test with cuproine remains positive, but, on further dilution, will become negative. The rate of dilution given by the distances: x_1z_1, x_2z_2, x_3z_3, etc. must be related to the percentage of copper in the different possible mixtures. This relation is exactly given by the figure; tables or diagrams are given by the procedure to find the unknown percentage in function of the dilution.

WENGER in Geneva and CLAEYS in Ghent have devised independently procedures based on this principle for the rapid semi-quantitative analysis of Cr-Ni steel[6].

Semi-quantitative analyses can be carried out with simple apparatus (drop plates, pipettes, and a few reagents), very rapidly, with good reproducibility and an accuracy of several per cent. In trace analysis a large sample (line $a + c$ = constant situated as low as possible) and a very sensitive test (line PS as high as possible) are favourable, allowing fairly good results with this practice. For high percentages the results are poor because the distances x_4z_4 and x_5z_5 are about the same.

NEW ORGANIC REAGENTS

1. The general objective

The work done, initially, for the "Commission on Analytical Reactions", consisted in the selection and experimental control of well-defined tests in the pure state and in presence of interfering substances. The new reagents were in the majority organic compounds and we all know the extent to which application of organic reagents has been developed in the last few decades, this being the reason why the I.U.P.A.C. decided on the creation of the Committee. We are also well aware of the fundamental researches done, for instance by FEIGL and his co-workers[1], to improve the applicability of organic reagents, by the introduction in the molecule of definite groups, modifying the solubility or the colour of the compounds formed.

We were interested in the same problem and, apart from finding conditions rendering a test "specific", synthesised new derivatives of definite organic compounds containing characteristic groupings in order to enhance the sensitivity and in order to get a better understanding of what is structurally needed to obtain a restricted selectivity with some elements of the periodic system.

2. *New fluorone-derivatives*

We have synthesized the 2,3,7-trihydroxy-6-fluorones in which the hydrogen-atom in position 9 was replaced respectively by: methyl, phenyl, *o*-hydroxy, *m*-hydroxy, *p*-hydroxy-phenyl and *m*, *p*-dihydroxy-phenyl. We will give them the trivial names: methylfluorone, phenylfluorone, *o*-hydroxyphenylfluorone, and so on.

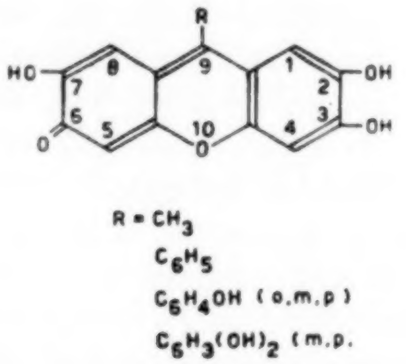


Fig. 7

TABLE I

Metal	Methyl	Phenyl	*o*-Hydroxy	*m*-Hydroxy	*p*-Hydroxy	Dihydroxy (*m*, *p*)
Sb^{III}	Bright-red*	Carmine*	Orange-red*	Carmine*	Bright red*	Bright red*
$Sn^{II,\ IV}$	Yellow	Orange*	Orange	Orange	Orange	Yellow
Ge	Orange*	Orange-red*	Orange*	Orange*	Orange*	Orange-brown
Mo	Brown-red*	Bright red*	Dark red*	Bright red*	Bright red*	Red-brown*
V	Gray*	Black-brown*	Brown*	Gray-brown*	Black*	Brown*
Fe^{III}	Yellow	Orange	Yellow	Yellow	Yellow	Yellow
Ti	Yellow	Pink*	Yellow	Yellow	Orange	Yellow
Zr	Orange	Orange-red*	Yellow	Orange	Yellow	Yellow

Methylfluorone had been studied by WENGER and his co-workers and described as a selective reagent for Sb(III).

We improved the preparation and purification of methylfluorone and established the conditions under which antimony can be detected with great selectivity by means of a spot reaction on filter paper impregnated with the reagent.

The comparative study of the synthesised fluorones is resumed in Table I, in which the colour of the compound and the formation of a precipitate (indicated by an asterisk) are given for the selective group of reacting metals.

It may be noticed that all the precipitates are formed in 1 *N* hydrochloric acid and that they resist decomposition in stronger solution. The germanium precipitate for instance is not decomposed by 11 *N* acid, while the other precipitates are dissolved in 6 *N* hydrochloric or nitric acid. The compounds formed with molybdenum, antimony and vanadium are also very stable in acid solution.

It was possible, by slight modifications of the working conditions, to realise a specific procedure for the detection of germanium with phenylfluorone and of molybdenum with *o*-hydroxyphenylfluorone. This last reagent even permits a specific detection of Cu(II), giving an intense violet precipitate, in a procedure where the other metals are without influence.

This study proved fruitful in connection with the analytical chemistry of germanium, from a practical as well as from an academic standpoint.

Phenylfluorone may be considered as a very sensitive reagent for germanium, for qualitative as well as for quantitative purposes. It was used with success by CLULEY[7] for the absorptiometric determination of germanium, the colour being developed in HCl solution in presence of arabic gum. After 30 minutes the colour is completely developed and remains constant for at least 14 hours.

CLULEY pointed out that the method had a considerable number of advantages in comparison with the gravimetric tannin method for the determination of germanium in flue dust, coal and coke.

From an academic standpoint the fluorones are even more interesting compounds, because the molecule is both an *ortho*diphenol and a quinone. It results namely from a very interesting study of BÉVILLARD[8] that an organic molecule presenting an *ortho*phenolic form and a quinonoid form, either simultaneously or due to a prototropic phenomenon, precipitates germanium in strong acid medium.

The study of BÉVILLARD opens new analytical possibilities for the gravimetric or absorptiometric determination of germanium and is also of significance for some other elements: Sn(IV),Sb(III),V(V),Zr(IV),Ti(IV) and Mo(VI).

It would perhaps be very promising to study the order of stability of these different metal complexes and to use this for the rational application of the fluorones in analytical separations of distinct metals or, by the use of those metals, to confirm the presence of diphenolic and quinonoid groups in organic structures.

3. New aromatic diamino compounds

Diamino aromatic compounds give in general coloured compounds with oxidising ions. The reaction of 4,4′-diaminodiphenyl (or benzidine) with V(V) for instance is well known as a result of the investigations of FEIGL and co-workers.

After having studied other diamino-diphenyl derivatives in their reactivity with different ions, we found that diaminobenzidine gives a yellow precipitate with Se(IV), the reaction being (Fig. 8):

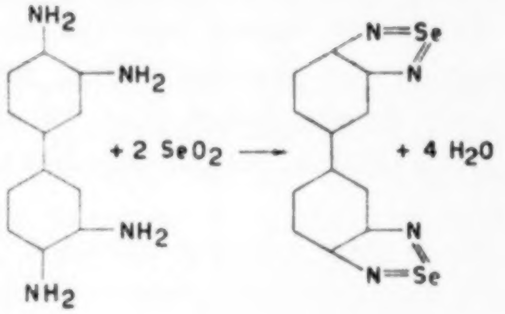


Fig. 8

Analogous reactions are given by *o*-phenylenediamine, *o*-toluylenediamine and peri-naphthalenediamine, the compounds formed having been described by HINSBERG[9], in 1919, and called by him piazselenole.

The selenodiazol studied by us allows the identification of selenium in presence of tellurium. We found a sensitivity, in a micro-test tube, of pD = 6. Furthermore, the precipitate can be used for the microgravimetry of Se(IV) and allows its absorptiometric determination.

The diaminobenzidine can be obtained in a very pure state by a procedure due to PIEN[10] and can also be used for the determination of diacetyl in butter. It forms an interesting reagent for the detection and determination of Se.

4. Derivatives of polypyridine and of phenanthroline

When one of my co-workers, Dr. J. HOSTE began his work on the reaction of monovalent copper with organic molecules of the type of 2,2′-dipyridyl and 1,10-phenanthroline, these compounds were in use essentially as iron-"specific" reagents in the ferroinreaction. SMITH and co-workers[11] had published their outstanding researches on numerous substituted derivatives of these compounds, focussing their attention on the formation of complex divalent cations, in the first instance with ferrous iron.

In a study, published in *Analytica Chimica Acta*[12], in the first pages of the volume of 1950, HOSTE called the attention to the copper-"specific" grouping of 2,2′-dipyridyl and 1,10-phenanthroline and of related molecules, with the same characteristic ferroin reaction group (= N — C — C — N =), but lacking the property of giving a coloured chelated cation with ferrous iron.

Extending the work of BRECKENRIDGE and co-workers[13] on 2,2′-diquinolyl, HOSTE found that the Cu(I) chelated complex of this compound, soluble in alcohol with an intense purple colour, was extractible in non-miscible alcoholic solvents, like *iso*amyl alcohol. He made use of this property to devise a very sensitive and specific reaction for copper, all other ions, for instance coloured like Co,Ni and even Fe,being without influence. It was puzzling that 2,2′-diquinolyl, although containing the ferroin reaction group, gave no coloured compound with ferrous iron.

It was known that complexes with the formula ML_3^{+2}, where M is a bivalent metal ion like Fe, Cd, Zn, Ni, Cu or Ru and L a ligand polypyridyl or phenanthroline molecule, could be formed, and that dipyridyl and phenanthroline were able to react with monovalent copper, as described first by Tartarini[14] and later by Moss and Mellon[15].

Tartarini found that the brown-red complexes of monovalent copper with dipyridyl or phenanthroline, insoluble in water, had the composition CuL_1^+. Hoste demonstrated that, in alcoholic solution, in which these complexes are readily soluble, copper coordinates two molecules of the ligand, giving the cation CuL_2^+.

Since three types of chelated cations: CuL_1^+, CuL_2^+ and FeL_3^{+2} are formed with dipyridyl and phenanthroline, what could be the reason for the trichelated 2,2′-diquinolyl complex of ferrous iron not being formed?

In an attempt to find a solution to this puzzle, Hoste investigated eight organic molecules, some of them being new and specially synthesised for this purpose, containing the characteristic grouping =N—C—C—N=. He studied their reaction with monovalent copper or with ferrous iron[12].

Smith and co-workers[11] knew also that the 2,9-dimethyl-1,10-phenanthrolines

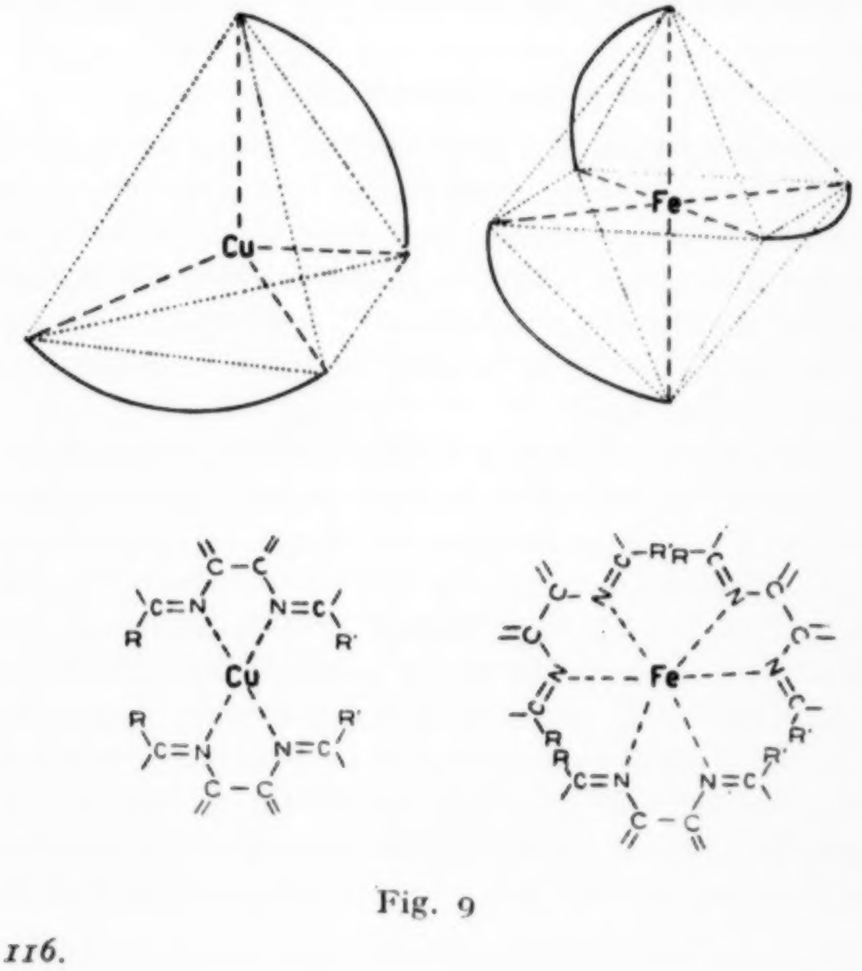


Fig. 9

were not able to give the ferroin reaction and omitted those derivatives from their list of 25 mono- and poly-methyl derivatives of 1,10-phenanthroline studied for their typical ferroin reaction.

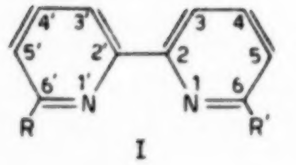
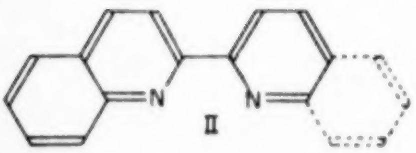
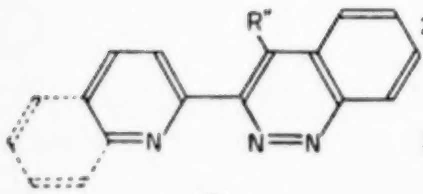
The solution of the puzzle was that, when the characteristic grouping C=N—C—C—N=C has attached at its extremities groups R or R′ or their equivalent, one or two atoms incorporated into quinolyl rings, the formation of the trichelated cation FeL_3^{+2} is sterically hindered, as can be explained by the following consideration (see also Fig. 9):

The bivalent iron, in the FeL_3^{+2} cation, is six-coordinated, the three ligands being chelated in octahedral configuration. If these ligands are substituted in both α-positions, the corresponding spatial model permits us to see that three ligands can no longer be bound, without reciprocal hindrance, in octahedral relation.

This point of view is confirmed by the fact that substitution of one α-position, as for instance in 6-methyl-2,2′-dipyridyl and in 2-methylphenanthroline, greatly weakens the intensity of the colour of FeL_3^{+2} complex. It furthermore appears that, when one α-position is blocked by a bigger substituent, as is

TABLE II

DERIVATIVES CONNECTED WITH 2,2′-DIPYRIDYL

		CuL_2^+		FeL_3^{+2}	
		E	λ	E	λ
 I	R = R′ = H 2,2′-dipyridyl	4550	435	8930	522
	R = R′ = CH_3 (J. Hoste)	6570	455	—	—
 II	2-pyridyl-2′-quinolyl (J. Hoste)	5780	490	—	—
	2,2′-diquinolyl "Cuproine" (J. Hoste)	6590	546	—	—
 III	2′-quinolyl-3-cinnolyl (H. Irving)	8500	485	—	—
	2′-pyridyl-3-cinnolyl (H. Irving) R″ = p-MeO C_6H_5	?	?	18200	530

the case in 2-pyridyl-2′-quinolyl, formation of the FeL_3^{+2} complex is sterically hindered.

For the CuL_2^+ cation, on the contrary, the spatial model being tetrahedral, with copper four-coordinated, two chelated ligands, even with substitution in α-position, cannot exert reciprocal hindrance. This situation favours the formation of the dichelated CuL_2^+ cation, with all ligands containing the characteristic grouping

$$R{-}C{=}N{-}C{-}C{-}N{=}R'.$$

For a practical reason, namely the ease with which it can be prepared, 2,2′-diquinolyl was chosen by HOSTE at that time as the most attractive copper reagent and named by him "cuproine".

Since then we used the reagent for the absorptiometric determination of copper in water, in steel, in biological material, for instance in plant ashes and in blood serum after dry or wet destruction. The copper level in blood in humans and its variation with the iron content in cases of anaemia was determined in an extensive research by means of cuproine.

This last problem, determination of the iron content of blood serum in presence of copper, initiated a new research, namely the use of phenanthroline-methyl-derivatives, in the determination of iron by extraction with organic non-miscible solvents. HOSTE succeeded in the extraction of iron by means of 3,5,6,8-tetramethyl-1,10-phenanthroline, in *iso*amyl alcohol or in chloroform, in presence of perchlorate or cyanide anions, and described a procedure for the absorptiometric determination of iron at very low concentrations, between 0.04 and 1 μg/ml.

The study of the iron"specific" and the copper"specific" groupings has made considerable progress during the last two years.

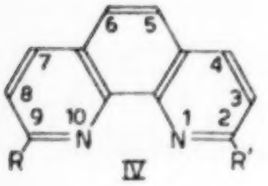
SMITH and his co-workers, having prepared 25 mono-,di-,tri- and tetra-methyl derivatives of 1:10-phenanthroline and having studied the effect of methyl group substitutions on physical constants, like molecular extinction coefficient and redox potentials of ferrous complexes of these derivatives, were in a good position to investigate the cuprous complexes of the corresponding methyl-substituted phenanthrolines and of one diphenyl-derivative, namely the 4,7-diphenyl-1,10 -phenanthroline[11]. (see Table III: formula V)

This work considerably extends the study of the "cuproine"-reaction as a result of the researches of HOSTE. The achievements on the "ferroin"-reaction completes a brilliant example of the analytical possibilities offered, by substitution, on physical and chemical properties of reagents having the same functional group.

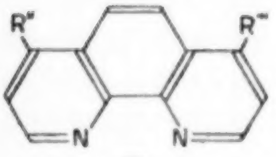
SMITH AND MCCURDY have investigated 28 methyl derivatives of 1,10-phenanthroline forming bichelated cuprous cations CuL_2^+ and listed the pH values governing the first formation of the coloured complex and the range of pH of its stability. They determined the wavelength of maximum absorption for each cation as well as their molecular extinction coefficient. They found simple rules to predict

TABLE III

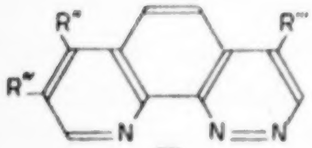
DERIVATIVES CONNECTED WITH 1,10-PHENANTHROLINE



IV



V



VI

	CuL_2^+		FeL_3^{+2}	
	E	λ	E	λ
$R = R' = H$ 1,10 phenanthroline	7040	435	11000	510
$R = R' = CH_3$ "neo-cuproine" (G. F. Smith)	7950	455	—	—
$R = CH_3$; $R' = H$ (H. Irving)	?	?	600	400
$R'' = R''' = CH_3$ (G. F. Smith)	8980	437	14000	512
$R'' = R''' = C_6H_5$ (G. F. Smith)	12100	458	22390	533
$R'' = OH$; $R''' = CH_3$ $R'''' = -COOC_2H_5$ (H. Irving)	?	?	14600	605

the wavelength of maximum absorption for each substituted methyl derivative, the average deviation between calculated and measured values being less than one per cent. The predictions for the molecular extinction coefficient were somewhat less accurate, although with an agreement of ± 20%. Nevertheless this gives a fair degree of certainty, quite sufficient for qualitative predictions of this physical constant.

Substitution of phenyl instead of methyl in the 4,7-position produced an increase in the wavelength of maximum absorption of 23 mμ for the "cuproine" as well as for the "ferroin"-complexes, while the increase in the molecular extinction coefficient for both complexes is about double the value of unsubstituted 1,10-phenanthroline. This makes the 4,7,-diphenyl-1,10-phenanthroline, named "bathophenanthroline", a very valuable new reagent for monovalent copper and for bivalent iron. As was found by SMITH, DIEHL AND MCCURDY the coloured bathophenanthroline "cuproine" and "ferroin" complexes are both extractible in *iso*amyl alcohol, but, by bringing the pH at 4, the CuL_2^+ cation is converted in the colourless mono-complex CuL_1^+, so that, under these conditions, iron can be determined without interference of copper. The very high molecular extinction coefficient of the bathophenanthroline-ferrous complex, namely 22.390, provides the most sensitive detection and absorptiometric determination of iron in presence of copper.

References p. 116.

It is clear that a further study, along the same lines, of other derivatives of 1,10-phenanthroline will bring in the near future copper and iron reagents even superior to bathophenanthroline, at the present time the best of all.

According to the same general principles IRVING and co-workers made important contributions to the study of the essential factors governing the selectivity of organic reagents and investigated also the "ferroin"-complexes as they become only "cuproine"-complexes by steric hindrance.

They determined the orders of stability of complexes of bivalent Mn,Fe,Co,Cu and Zn with ethylenediamine and found the normal order (log $\mathbf{k}_1$ = 2.73; 4.28; 5.89; 10.55; 12.09, respectively), the normal IRVING-WILLIAMS stability sequence. But as soon as the grouping N—C—C—N is incorporated in an aromatic system, they found a large increase in the strength of the ferrous complex, namely iron close to bivalent copper for 2-2′-dipyridyl as ligand or iron close to zinc for 1,10-phenanthroline as ligand. This goes hand in hand with the development of a strong absorption band (molecular absorption coefficient 8930 at 522 mμ for dipyridyl and respectively 11000 at 510 mμ for phenanthroline) (see Tables II and III). The singular position of iron in the order of stability of those bivalent metals was confirmed by IRVING when a — N : N — grouping is incorporated in the pyridine—or phenanthroline—molecule, as it happens when one makes use of cinnoline (2-azaquinoline) instead of quinoline. As cinnoline absorbs at longer wavelengths than quinoline the corresponding "ferroin"-aza-derivative investigated by IRVING, namely 3-carbethoxy-4-hydroxy-7-methyl pyrido(3,2$_{\mathrm{H}'}$) cinnoline (see formula VI on table III), has a *blue* colour instead of the well-known *red* colour (log k_3 = 15 ; E = 14,600 at $\lambda_{\max}$ = 605 mμ), while another aza-derivative, connected with dipyridyl, namely 3-(2′-pyridyl)-4-*p*-methoxyphenyl-cinnoline (see formula III on table II) gives a *red* $\mathrm{FeL_3}^{+2}$ cation (log k_3 = 15; E = 18,200 at $\lambda_{\max}$ = 530 mμ). This substance, with a phenylgroup in para-position to the nitrogen atom in the cinnoline ring, shows a marked increase in molecular extinction coefficient compared with the other ferroin complexes, a result confirming predictions made by IRVING, and constitutes, after bathophenanthroline prepared by SMITH, the most sensitive reagent for iron.

Other successes are predicted by IRVING as iron-singular reagents, by annelation in positions 4,5 and 4′,5′ in dipyridine (to give 3,3′-di-*iso*quinolyl, the *iso*-compound of "cuproine" used by HOSTE as reagent on monovalent copper) or in positions 3,4 and 7,8 in *o*-phenanthroline. Those new reagents, once prepared and investigated, will be superior to dipyridyle or phenanthroline, because their ferrous complexes will be more soluble in polar solvents and will permit a further refinement of the procedure initiated by HOSTE for the extraction of iron by means of derivatives of methylphenanthroline in solvents like *iso*amyl alcohol or chloroform[12].

We can say that the search for the best ligand of the ferroin-type to be used as reagent for iron is far from being complete at the present time but that the prospects are even more attractive and stimulating than before.

In the same direction the best ligand of the cuproin-type to be used as reagent for monovalent copper is not yet found. Diquinolyl (see formula II in Table II) was proposed first under the name of "cuproine" by HOSTE; 2,9-dimethyl-1,10-phenanthroline (see formula IV in Table III) was proposed by SMITH under the name of "neo-cuproine" and a new quinolyl-cinnolyl (see formula III in Table II) reagent is proposed now by IRVING, the respective molecular extinction coefficients beings: 6590, 7950 and 8500. Higher values were attained also by SMITH (see Table III). Here also changes in the nature of the ligand will bring further improvements in the future.

5. *Future developments in devising new reagents*

One can say that analytical chemistry will be developed along new paths in the coming years. The time is now over when new organic reagents will be discovered only on an empirical way.

Researches such as those concerned with ferroin and cuproine complexes indicate that predictions are possible regarding the structure of the ligand. Investigations on the order of stability of metal complexes, on the influence of position and nature of substituents on solubility (in water or in non-miscible solvents), on colour (molecular extinction coefficient and wavelength of maximum absorption), on steric hindrance enhancing selectivity, will be of fundamental significance in the search for new or better reagents. The synthesis of new organic compounds with the most promising analytical properties will be guided by schools like those of BJERRUM in Copenhagen[16], SMITH in Illinois, FREISER in Pittsburgh[17], IRVING in Oxford[18], SCHWARZENBACH in Zurich[19], and CALVIN in Berkeley (California[20]) and similar schools.

In devising new analytical reagents empiricism will no longer be the guide, but the complete cooperation of inorganic, organic and physical chemistry will be necessary to forge the best tools and weapons in the arsenal of analytical chemistry.

SELECTIVITY OF ANALYTICAL REAGENTS

Let us consider, in a last paragraph, the signification of the terms "selective" and "specific", as they are given by the definitions adopted, in 1937, by the Committee on New Analytical Reaction and Reagents.

The term specific referred to reactions (reagents) which, under certain test conditions, are *quite unambiguous* for *one* component; the term "selective" referred to reactions for more than one component.

The studies on the selectivity of organic reagents, for instance those of IRVING, have now taught us, by the theoretical study of reactions between metal-ions and chelating ligands, that the most that could be realised, with chelated compounds, could be a certain restricted selectivity; to find a chelating reagent that reacted with one metal-ion only was beyond reach.

If a few ions of comparable size, ionisation potential, valency, position in the periodic system, form chelated compounds of exceptional characteristics, as proved by some feature, like stability-, solubility-, or extinction-constant, IRVING proposes to distinguish these compounds by the term "singular". This proposal is worth considering, but its significance is entirely on the academic side, although for the moment.

Nevertheless a reagent giving "singular-compounds" with a few elements as proved by a theoretical study, would need to be rendered specific for only one of them, a procedure eradicating the influence of all the others. By "masking", "scavenging", "inactivating", an appropriate test could be made "specific" in a practical sense.

It is clear that, with this interpretation and referring to the words "under certain test conditions", the definition of the term "specific", as expressed by the Commission in 1937, is still appropriate and is to be maintained. In a practical sense specific tests do exist.

To resume, if the term singular-compound seems promising for theoretical purposes, the terms specific and selective maintain their definitions and their practical significance.

I am convinced that analytical chemistry will benefit more and more from theoretical studies on chelated compounds and that the most singular of them, in general, will be of great help in restricting the selectivity and in reaching the goal of specificity.

I believe that this aspect of the analytical chemistry is part of the scope of the Commission on Analytical Reactions and that, in collaboration with the Commission on Physico-Chemical Data of Analytical Interest and the Commission on Terminology, the Analytical Section of the I.U.P.A.C. can contribute to the promotion of research both in theoretical and in practical directions.

SUMMARY

The researches undertaken by the author for the "Commission of Analytical Reactions" of the International Union of Pure and Applied Chemistry are set out on broad lines.

One result has been the graphical representation of the sensitivity of the analytical reactions with the aid of sensitivity-diagrams. The practical use of the latter is illustrated by the determination of the impurities in commercial compounds (*e.g.* cooking-salt) or by the semiquantitative determination of certain elements (*e.g.* Ni and Cr) in special steels.

A second important series of work has led to new organic reagents which, under certain conditions, have been rendered specific.

New fluorone derivatives have been synthesised and have furnished interesting reagents. Thus phenylfluorone is an excellent reagent for germanium.

Diaminobenzidine is a good reagent for selenium.

The reaction of monovalent copper with diquinolyl has been the basis for research on the characteristic group $=N-C-C-N=$ contained in molecules such as 1,10-phenanthroline and *α-α'*-dipyridyl, reagents for ferrous and cuprous ions. A survey of the actual state of our knowledge concerning the reactions of ferroin and cuproin

References p. 116.

shows that, in future, the choice of the best analytical reagents will be foreseen and will be based on the physical-chemical properties of organic molecules containing certain characteristic groups.

RÉSUMÉ

Les recherches entreprises par l'auteur pour la „Commission des Réactions Analytiques" de l'Union Internationale de Chimie Pure et Appliquée, sont exposées dans leurs grandes lignes.

Un premier résultat a été la représentation graphique de la sensibilité des réactions analytiques à l'aide de diagrammes de sensibilité. L'usage pratique de ceux-ci est illustré par la recherche des impuretés dans une substance commerciale (le sel de cuisine p. ex.) ou par le dosage semi-quantitatif de certains éléments (Ni et Cr p. ex.) dans les aciers spéciaux.

Une deuxième série importante de travaux a conduit à de nouveaux réactifs organiques, qui, dans certaines conditions, ont pu être rendus spécifiques.

De nouveaux dérivés des fluorones ont été synthétisés et ont fourni des réactifs intéressants. Ainsi la phénylfluorone p. ex. constitue un réactif excellent du germanium.

La diaminobenzidine d'autre part s'est révélée comme un bon réactif du sélénium.

La réaction du cuivre monovalent avec le diquinolyle a été le point de départ de recherches sur le groupement caractéristique =N—C—C—N= contenu dans des molécules telles que la 1,10-phenanthroline et l'α-α'-dipyridyle, réactifs des ions fer(II) et cuivre(I). Un aperçu de l'état actuel de nos connaissances relatives aux réactions de la ferroïne et de la cuproïne, montre, qu'à l'avenir, le choix des meilleurs réactifs analytiques pourra être prévu et basé sur les propriétés physico-chimiques des molécules organiques renfermant certains groupements caractéristiques.

ZUSAMMENFASSUNG

Die von dem Autor für die „Kommission für analytische Reaktionen" der Internationalen Union für Reine und Angewandte Chemie vorgenommenen Untersuchungen werden in grossen Zügen dargelegt.

Das erste Ergebnis war die graphische Darstellung der Empfindlichkeit analytischer Reaktionen mit Hilfe von Empfindlichkeitsdiagrammen. Ihre praktische Anwendung wird durch die Untersuchung der Verunreinigungen von Handelsprodukten (z.B. des Kochsalzes) oder durch die halbquantitative Bestimmung gewisser Elemente (z.B. Ni und Cr) in Spezialstählen erläutert.

Eine zweite, wichtige Reihe von Arbeiten führte zu neuen organischen Reagenzien, die unter gewissen Bedingungen spezifisch gemacht werden können.

Neue Derivate des Fluorons wurden synthetisiert und lieferten interessante Reagenzien. So bildet z.B. das Phenylfluoron ein ausgezeichnetes Reagenz auf Germanium. Auf der anderen Seite hat sich das Diaminobenzidin als ein gutes Reagenz für Selenium erwiesen.

Die Reaktion des einwertigen Kupfers mit Diquinoyl war der Ausgangspunkt für Untersuchungen mit der charakteristischen Gruppe =N—C—C—N=, wie sie in Molekülen wie 1,10 - Phenanthrolin und $\alpha.\alpha'$-Dipyridyl, den Reagenzien auf Eisen- und Kupferionen, vorkommt. Eine Übersicht über den augenblicklichen Stand unserer Kenntnisse bezüglich der Eisen- und Kupferreaktionen zeigt, dass in der Zukunft die Auswahl der besten analytischen Reagenzien vorausgesagt werden könnte und auf die physikalisch-chemischen Eigenschaften von gewisse charakteristische Gruppierungen enthaltende organische Verbindungen gegründet werden könnte.

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ALIZARIN BLUE AS A SELECTIVE REAGENT FOR TRACES OF COPPER[*]

by

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It is now generally accepted that the specific and selective action of organic reagents depends upon the presence and position of certain atom groups. These groups are salt formers capable of forming coordination compounds (addition and chelate compounds). Based on this consideration, a certain amount of progress has been achieved. It has been possible to obtain a better understanding of the action of well-established reagents as well as to find organic compounds which can be used as precipitating, colour and masking reagents[1]. It must be pointed out that it is not merely the presence and position of certain groups which determine the analytical value of an organic compound. Very important factors are: the behaviour of the reagent and reagent products towards solvents; the pH, the temperature, and other essential reaction conditions. Furthermore, it is essential to analyse the influence of other atom groups present in the molecule of the reagent. Such groups are often capable of changing the solubility or colour, as well as the basic or acidic character of the groups.

In view of these facts it seemed of interest to test the behaviour of an organic compound, the molecule of which contains two characteristic atom groups. Such a compound is the blue-red dye alizarin blue, the synthesis and structure of which was established by AUERBACH[2].

A comparison between the formulas of alizarin blue (I), of alizarin (II) and 8-hydroxyquinoline (III) shows that the reacting groups of alizarin and 8-hydroxyquinoline are present in the molecule of alizarin blue.

According to I-III alizarin blue should possess the analytical properties of both alizarin and 8-hydroxyquinoline if the activities of its functional groups are unchanged. This means that alizarin blue, like alizarin, should form colour lakes, and like 8-hydroxyquinoline should form inner complex salts. However, this is not quite the case. It was observed that alizarin blue has no longer the

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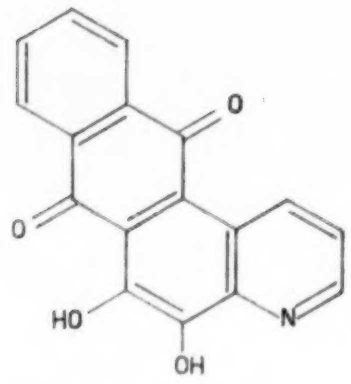
[*] Read at the Symposium on Analytical Chemistry, held at the University of Birmingham, England, Sept. 11th and 12th 1952.



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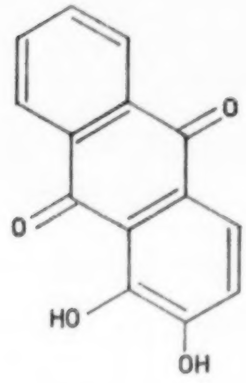

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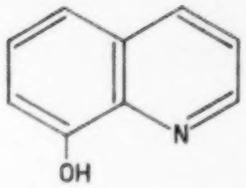
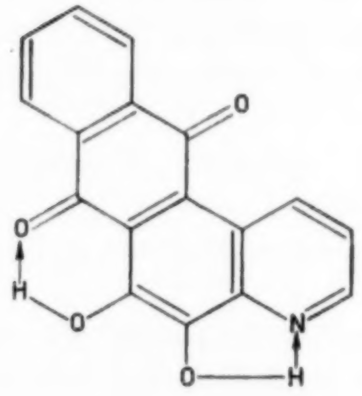


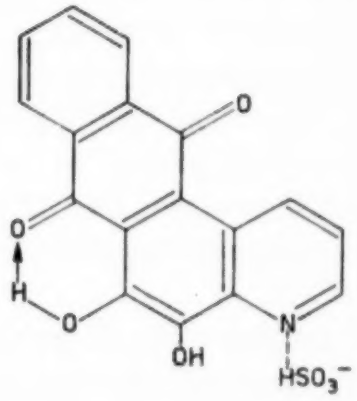
III

phenolic properties of compounds I and II; it is insoluble in alkali hydroxide. Furthermore, it is not dissolved by dilute acids, contrary to what would be expected of a derivative of quinoline. The loss of acidic and basic properties of alizarin blue is probably due to chelate formation, as shown in formula IV. This would account for the unexpected insolubilities*.

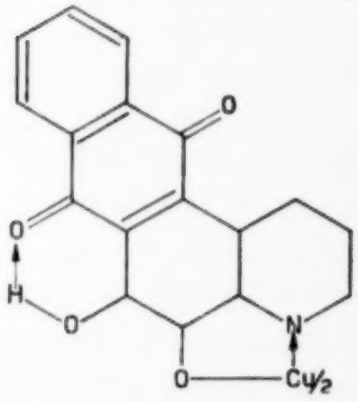
Alizarin blue is only soluble in concentrated sulphuric acid (less in concentrated hydrochloric acid) as well as in solution of alkali bisulphites. There exists an addition compound between one mole of the dye and two moles of sodium bisulphite; this so-called "Alizarin Blue S" probably contains an ionic bonded dye, as shown by formula V. Aqueous solutions of alizarin blue S are not stable; the free dye precipitates, especially when the solution is heated. The same occurs when solutions of the dye in concentrated mineral acids are diluted.



IV



V



VI

In its behaviour towards methyl and ethyl alcohol as well as acetone, alizarin blue differs from both alizarin and 8-hydroxyquinoline; it is insoluble in these liquids, which are generally used as solvents for organic reagents.

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* Insolubility of substituted phenols in alkali hydroxide was first observed by R. ADAMS, *J. Am. Chem. Soc.*, 41 (1919) 247, and attributed to their great water insolubility.

References p. 121.

Owing to lack of an appropriate solvent it is impossible to compare, under the same conditions, the analytical behaviour of alizarin blue, alizarin and 8-hydroxyquinoline respectively.

Two indications, however, point to the fact that alizarin blue still shows analytical properties of both 8-hydroxyquinoline and alizarin. AUERBACH (*loc. cit.*) has observed the precipitation of a blue copper salt from strong sulphuric acid solution, the salt containing two molecules of the dye to one atom of copper. For this compound, by analogy with the inner complex copper salt of 8-hydroxyquinoline, the chelate formula VI seems probable. DE BOER[3] has found that alizarin blue, by analogy with alizarin, forms colour lakes with acidic solutions of zirconium and hafnium salts, which can be decomposed by fluoride ions. The findings of AUERBACH and DE BOER indicate that alizarin blue reacts with the identical atom groups of both 8-hydroxyquinoline and alizarin only in strongly acidic solutions. It is well known that the last two compounds are non-selective reagents in weakly acid and alkaline solution. It is obvious that alizarin blue, because of its restricted solubility can, if at all, only react in strong acidic solution. In spite of this handicap, it seems that the incorporation of the functional groups of alizarin and 8-hydroxyquinoline into the larger molecule increases the selectivity of this reagent.

The copper salt of alizarin blue is particularly interesting because of its insolubility in strong acids. The salt is formed even by the action of alizarin blue on the acid-resistant innercomplex copper cupferronate. The fact that copper alizarin blue is an innercomplex salt with four chelate rings in the molecule (compare formula VI) may be connected with the extraordinary insolubility.

In order to make use of the formation of copper alizarin blue for the detection of copper it was necessary to prevent coprecipitation of the dye, as well as to avoid the colour of the reagent solution making it impossible to observe small quantities of the precipitated copper salt. This rather difficult problem was solved by making use of the following effects. The dye is soluble up to 0.2 % in pyridine, and this solution reacts readily with the solid or dissolved copper salts. Furthermore the dye obtained on evaporation of its pyridine solution is completely destroyed by acetic anhydride, whereby a colourless solution results. The copper alizarin blue, however, remains unaltered when treated with acetic anhydride. Based on these effects, a spot test for copper is possible which is much more sensitive than all selective spot tests for copper hitherto used.

Under these conditions only nickel interferes forming a blue solution*. In order to test for copper in the presence of nickel, it is necessary to form copper cupferronate and to extract the latter with chloroform. After the evaporation of chloroform the reaction with alizarin blue can be used. In this way it is also possible to detect traces of copper in water.

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* It was thus far not possible to isolate a nickel alizarin blue in pure form.

I. SPOT REACTION FOR COPPER

Procedure. One drop of the test solution is evaporated to dryness on a porcelain spot plate. Without allowing the residue to cool, a drop of a saturated solution of alizarin blue in pyridine is added. The pyridine is evaporated and 1-2 drops of acetic anhydride are added. In the presence of copper, a blue residue is obtained. It is characteristic that small amounts of copper alizarin blue adhere so strongly to the spot plate that they cannot be washed away with water. This is particularly useful for the detection of very small amounts of copper.

Limit of identification: 0.0025 γ copper

Concentration limit: 1 : 20 000 000

II. DETECTION OF TRACES OF COPPER IN WATER

Procedure. 100 ml of water are acidified with dilute hydrochloric acid. 1-2 drops of 6 % aqueous solution of cupferron are added and shaken with 5 ml of chloroform to extract the copper cupferronate formed. After the separation of the two layers, the chloroform is evaporated in a small crucible. The dry residue is tested according to procedure I. In this manner, 0.025 γ copper can be identified, corresponding to a dilution of 1 : 4 000 000 000.

III. DETECTION OF TRACES OF COPPER IN METALLIC NICKEL OR NICKEL SALTS

Procedure. From the material to be tested (metallic nickel or nickel salts) an amount is brought into solution corresponding to 0.1 g nickel, and the volume is brought to 100 ml by addition of water. 1-2 drops of 6 % aqueous solution of cupferron are then added and the same procedure is followed as previously described above for the detection of traces of copper in water. In 100 ml of 0.1 % nickel solution, an amount of 0.025 γ copper can be detected corresponding to a content of 0.000025 % copper in nickel.

IV. DETECTION OF TRACES OF COPPER IN GASOLINE

For the detection of copper in gasoline, a method was recommended[4] which is based on the formation of copper diphenylthiocarbazone. This test besides its non-selectivity is far less sensitive than the test with alizarin blue. In order to check the latter test, 0.025 γ copper in form of copper cupferronate was dissolved in 100 ml of gasoline. After evaporation of the gasoline, the copper could be identified with alizarin blue.

ACKNOWLEDGEMENT

The authors are indebted to the Conselho Nacional de Pesquisas (Brazil) for material assistance.

SUMMARY

A new test for copper has been developed based on the formation of a blue acid-resistant innercomplex salt of copper with the dye alizarin blue. The test is more sensitive than all other copper tests hitherto employed, including tests based on the catalytic action of copper ions. When carried out as a spot reaction a limit of identification of 0.0025 γ copper is attained. Procedures are described to detect copper in water (up to 1 : 10^9) and in nickel salts (up to 0.000025 %).

RÉSUMÉ

Une nouvelle réaction du cuivre est proposée, elle est basée sur la formation du complexe interne du cuivre avec le colorant bleu d'alizarine. Le bleu d'alizarine est plus sensible que tous les autres réactifs du cuivre employés jusqu'ici, y compris les réactions basées sur l'effet catalytique des ions cuivre. Par la technique ,,à la touche'' on peut arriver à la limite de perceptibilité de 0.0025 γ de cuivre. Des procédés sont décrits pour déceler le cuivre dans l'eau (jusqu'à 1 : 10^9) et dans les sels de nickel (jusqu'à 0.000025 %).

ZUSAMMENFASSUNG

Es wurde eine neue Kupferprobe entwickelt, die auf der Bildung eines blauen, säureresistenten, inneren Komplexsalzes des Kupfers mit dem Farbstoff Alizarinblau beruht. Diese Reaktion ist empfindlicher als alle anderen bisher verwendeten Kupferreaktionen, einschliesslich der Reaktionen, die auf der katalytischen Wirkung des Kupferions beruhen. Bei der Ausführung als Tüpfelreaktion erreicht man eine Grenzkonzentration von 0.0025 γ Cu. Es werden Verfahren beschrieben, um Kupfer in Wasser (bis zu 1 : 10^9) und in Nickelsalzen (bis zu 0.000025 %) zu bestimmen.

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SOME FACTORS INFLUENCING THE SOLUBILITIES OF AMINE SULPHATES*

by

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A well-established method for the determination of sulphate is based on its precipitation as the sparingly soluble benzidine salt. The determination can be completed gravimetrically, titrimetrically, colorimetrically or even manometrically, but whichever technique is employed, the accuracy of the method depends on the quantitative precipitation of sulphate ions. Benzidine sulphate, however, is soluble in water to the extent of 0.098 g/l[1], and, although this figure can be reduced considerably by the presence of an excess of the reagent, it nevertheless defines the limit of accuracy of the method. Furthermore, because the benzidine method is subject to interference arising from certain ions often associated with sulphate, it would be advantageous to have an alternative reagent free from these defects. Accordingly, an investigation was undertaken[2] to determine the interdependence of the molecular structures of amines related to benzidine and the solubilities of their sulphates.

The first line of approach was to examine the homologues of benzidine, in the hope that nuclearly substituted alkyl groups would exert the weighting effect commonly found in organic chemistry. It was found, however, that the introduction of an alkyl group raised the solubility of every amine sulphate examined. Since it is inconceivable that there should be no weighting effect, the obvious conclusion is that the introduction of alkyl groups must be associated with some other effect which opposes that due to the increase in molecular weight. The purpose of the present paper is to advance a tentative theory concerning this opposing effect, and to indicate that there exists at least one amine which has a sulphate less soluble than that of benzidine.

The increase in solubility following the introduction of an alkyl group could be due to electronic or stereochemical effects. In the former case, it would arise from the modification of the basicity of the amino groups, and should be greater if the substituents are in positions ortho to these groups.

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* Read at the Symposium on Analytical Chemistry, held in the University of Birmingham, England, Sept. 11-12, 1952, by the Midlands Society for Analytical Chemistry.

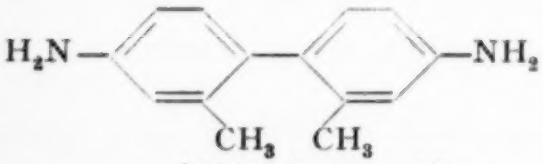
The stereochemical effects could result in an alteration of the crystal lattice energy. The solubility of a substance depends upon the crystal lattice energy, the solvation energy and the entropy of solution. For closely related compounds, the solvation energy and the entropy of solution are not likely to differ appreciably, but small changes in the molecular shape can have substantial effects on the crystal lattice energy, and, therefore, on the solubility.

The introduction of a nuclearly substituted alkyl group alters the molecular shape in two ways. Firstly, it forms a projection on the side of the molecule, thereby making it more difficult for other molecules to become adjacent in a crystal lattice. This factor should be largely independent of the position of the alkyl group. Secondly, an alkyl group inhibits free rotation about the bond joining the two rings, which cannot readily adopt the coplanar configuration known to exist in diphenyl derivatives in the solid state. That this holds for substituents in the 2-position has been shown by numerous workers using physical methods[3]. It is also shown by the fact that 2-alkylbenzidines cannot be oxidised to highly coloured meriquinoid substances, which definitely require the two rings to be coplanar. The hindrance due to a substituent in position 3 is, of course, much smaller, but its existence has been shown by electron diffraction[3]. Hence, there are three possible ways in which an alkyl group could render a sulphate more soluble. These are summarised below together with the criteria by which they may be distinguished.

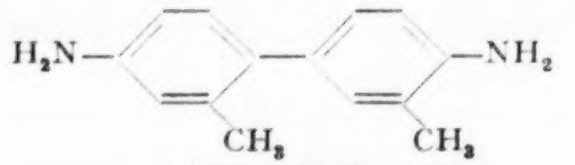
Effect	Position of Substituent
Electronic	$3 > 2$
Projection	$2 \bumpeq 3$
Rotation	$2 > 3$

It should be emphasized that the present authors do not attempt to prove that any of these effects does not exist. The purpose of this investigation is merely to determine the principal effects which appear to be active.

The following table shows some results obtained experimentally. Except where otherwise indicated, these results were obtained by BELCHER AND NUTTEN (*loc. cit.*).

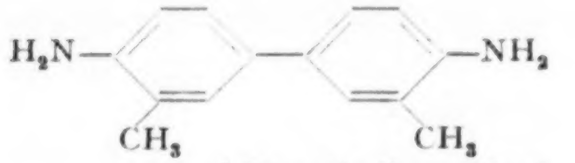
Amine	Solubility of Sulphate (at 25°C) g/l
 2 : 2′-Dimethylbenzidine	8·907

References p. 129.



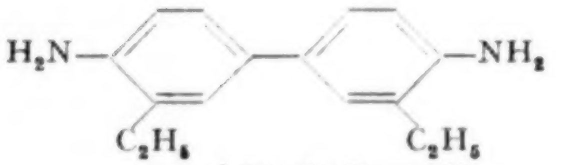
2 : 3′-Dimethylbenzidine

0·488



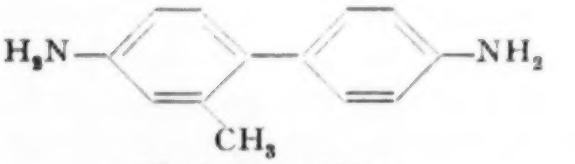
3 : 3′-Dimethylbenzidine[4]

0·3



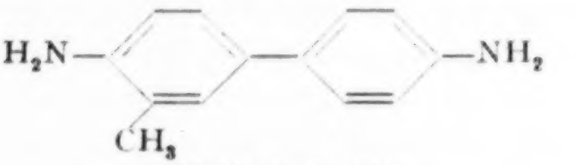
3 : 3′-Diethylbenzidine

0·429



2-Methylbenzidine

0·342

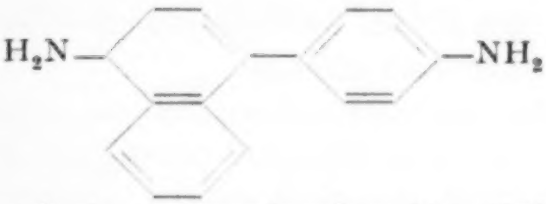
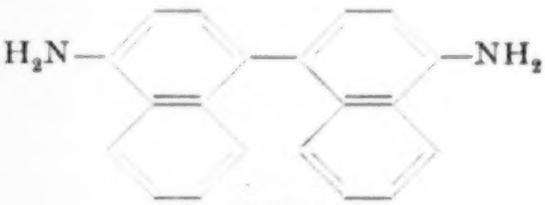
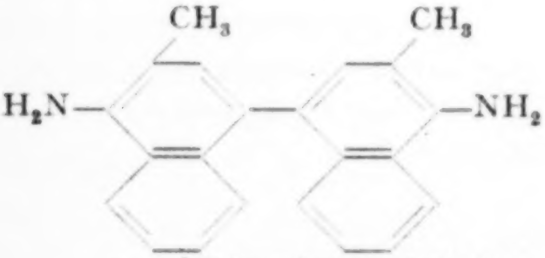


3-Methylbenzidine

0·448

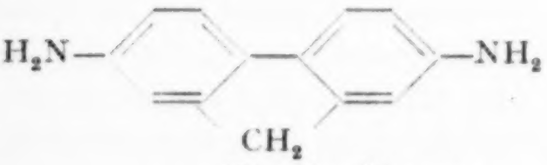
The first three of these results show that the effect of a methyl group is greater in a 2-position than in a 3-position. This indicates that the increased solubility is due to the inhibition of free rotation about the bond joining the two rings. As would be expected, the solubility of 2-methylbenzidine sulphate falls between the 2 : 3′- and 3 : 3′-dimethyl compounds. The solubility of 3 : 3′-diethylbenzidine sulphate is difficult to interpret. The steric effect of an ethyl group is greater than that of a methyl group. In aliphatic compounds, the same is true of their electronic effects, but in many aromatic compounds the reverse is the case, owing to hyperconjugation. If one postulates hyperconjugation in these molecules, the solubility of 3 : 3′-diethylbenzidine sulphate lends support to the stereochemical theory already expressed; otherwise, it neither supports nor contradicts it. 3-Methylbenzidine remains anomalous; it is significant that this is the only one of the amines so far examined which does not conform to the theory outlined in this paper.

If one of the benzene rings of the benzidine molecule be replaced by a naphthalene ring, the consequent restriction of free rotation will be smaller than that due to a methyl group in position 2. In addition, there will be a greater weighting effect, so that a low sulphate solubility might be expected. The resulting molecule will, however, have a peculiar asymmetry, and can hardly be expected to fit into a crystal lattice similar to that of benzidine sulphate. When molecular symmetry is restored, as in naphthidine, a very low sulphate solubility, comparable with that of benzidine, results. The introduction of alkyl groups into the naphthidine molecule serves only to restrict rotation further, and consequently to increase the sulphate solubility. This is shown by the following results.

Amine	Solubility of Sulphate (at 25°C) g/l
 4-Amino-1-(p-aminophenyl-)naphthalene	0·205
 Naphthidine	0·101
 3 : 3′-Dimethylnaphthidine	0·162

The solubility of naphthidine sulphate is only slightly higher than that of benzidine sulphate, and actually corresponds to a smaller concentration of sulphate ions in solution. Nevertheless naphthidine cannot be used as a reagent for the determination of sulphates, because of its insolubility in the conventional solvents.

Two amines with coplanar molecules have been investigated with the following results:

Amine	Solubility of Sulphate (at 25°C) g/l
 2 : 7-Diaminofluorene	0·175

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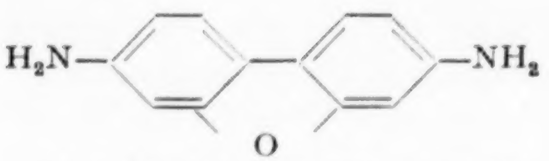
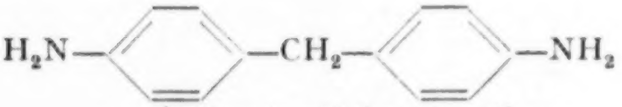
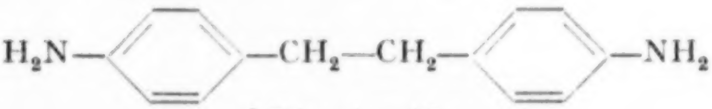
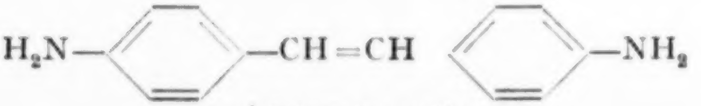
 2 : 7-Diaminodiphenylene oxide	0·218

For amines with coplanar molecules, these compounds appear to have rather soluble sulphates, so that another factor somewhat less important than coplanarity must exist. It will be seen at once that the two amines above show a distinct difference from benzidine. In the latter, the two amino groups and the carbon atoms in positions 4,1,1′ and 4′ are all collinear. This is not the case with the other two amines. It seems, therefore, that two conditions are necessary for low sulphate solubility: the two rings must be coplanar and collinear.

From the foregoing, it is clear that no nuclearly substituted benzidine can ever be a suitable reagent for the determination of sulphates. The only possibility of preparing such a reagent depends upon the insertion of certain groups between the two rings. Several compounds containing such groups have been examined, and provide confirmation of the theory.

Amine	Solubility of Sulphate (at 25°C) g/l
 4 : 4′-Diaminodiphenylmethane	17·53
 4 : 4′-Diaminodibenzyl	0·19
 4 : 4′-Diaminostilbene	0·132

4 : 4′-Diaminodiphenylmethane is neither coplanar nor collinear, and accordingly has a very high sulphate solubility. The solubility of 4 : 4′-diaminodibenzyl sulphate has now been determined. STELLING AND FITTIG^5 state that this compound is more soluble than benzidine sulphate, and experiments by the present authors confirm this finding. 4 : 4′-Diaminostilbene is coplanar but not collinear, and its sulphate solubility is, therefore, comparable with those of 2 : 7-diaminofluorene and 2 : 7-diaminodiphenylene oxide. 4 : 4′-diaminostilbene should exist in two stereoisomeric forms, but only one of these is known. The preparation of the other and the determination of its sulphate solubility would be of great interest.

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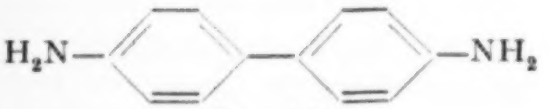
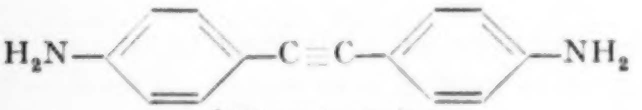
All these results confirm the theory, and it has been possible to design a molecule with a sulphate solubility smaller than that of benzidine.

If an acetylenic linkage be introduced between the two rings, the molecule will be collinear, and resonance will tend to make it coplanar. It is known that the hydrogen atoms in the 2-positions of the benzidine molecule offer a small but appreciable resistance to free rotation. Owing to the greater separation of the rings, this effect is very much diminished in the acetylenic compound. Further, the two carbon atoms introduced should give rise to a weighting effect. For these reasons, the compound in question, 4 : 4′-diaminotolane, should have a lower sulphate solubility than benzidine. We have proved this experimentally, thus supporting the theory outlined above.

Amine	Solubility of Sulphate (at 25°C) g/l
 Benzidine	0·098
 4 : 4′-Diaminotolane	0·059

The possibility of applying 4 : 4′-diaminotolane as an analytical reagent is at present being investigated.

The 4 : 4′-diaminotolane was prepared from 4 : 4′-dinitrostilbene dibromide by an improved version of the method of REINHARDT[6]. A new method was found for the preparation of 4 : 4′-dinitrostilbene dibromide.

EXPERIMENTAL

Preparation of 4:4′-dinitrostilbene dibromide

Dinitrostilbene (10 g) was suspended in dioxan. An excess of bromine was added to the warm suspension, and the mixture was boiled until as much as possible had gone into solution. After hot filtration, the filtrate was poured into an excess of water, when the crude product was precipitated. This was filtered, and used for the next stage without purification.

Preparation of 4:4′-dinitrotolane

4 : 4′-Dinitrostilbene dibromide (77 g) was suspended in methanol (500 ml), and a methanolic solution of potassium hydroxide (58 g in 150 ml) was added to the boiling mixture in the course of one hour. The mixture was boiled for a further forty-five minutes, and then filtered hot. The resulting solid was washed with ethanol and then water. The crude product was reduced as described below.

Preparation of 4 : 4′-diaminotolane

The crude product of the previous reaction was suspended in ethanol (350 ml), and zinc dust (70 g) was slowly added to the stirred mixture. The latter was then cooled, and hydrochloric acid (220 ml; d. 1.16) was added dropwise, the temperature not being allowed to exceed 20°C. The solution was stirred for a further eight hours at a temperature of 15-20°C. The mixture was decanted from the zinc dust, and filtered, the zinc dust and solid residue being washed with 50% ethanol. The combined filtrate and washings were treated with 25% sulphuric acid (100 ml). The resulting precipitate of 4 : 4′-diaminotolane sulphate was filtered, and then heated with an excess of sodium hydroxide solution. Filtration yielded 4 : 4′-diaminotolane.

Yield of crude product, 12 g.

A sample of the amine was recrystallised from acetone, but the recovery was poor. After two recrystallisations, the m.p. was 235°C. The compound contained C, 80.50%; H, 6.09%. 4 : 4′-Diaminotolane requires C, 80.74%; H, 5.81%. The diacetyl compound[7] was prepared by way of further characterisation.

Preparation of 4:4′-diacetamidotolane

4 : 4′-Diaminotolane (0.5 g) was heated with acetic anhydride (1 ml) on a water-bath for about 30 min. The product was poured into water, filtered and recrystallised from glacial acetic acid. M.P. 289°C. The product contained C, 73.89%; H, 5.70%. 4 : 4′-Diacetamidotolane requires C, 73.91%; H, 5.52%.

Preparation of 4:4′-diaminotolane sulphate

A little pure 4 : 4′-diaminotolane was dissolved in acetone, and the solution was cooled. A solution of a few drops of concentrated sulphuric acid in acetone was then added. The precipitated 4 : 4′-diaminotolane sulphate was filtered, and washed successively with water and acetone. It contained C, 54.96%; H, 4.92%; N, 8.89%; S, 10.7%. 4 : 4′-Diaminotolane sulphate requires C, 54.89%; H, 4.61%; N, 9.15%; S, 10.47%.

Determination of solubilities

The sulphate under examination was suspended in water contained in a conical flask immersed in a thermostat, and the suspension was stirred for forty-eight hours. A 100 ml portion of the solution was then withdrawn through a filter stick. The solution was placed in a weighed platinum dish, and evaporated to dryness on the steam bath, the dish being weighed afterwards.

ACKNOWLEDGEMENTS

We wish to record our thanks to Dr. W. **Wilson** for helpful suggestions with regard to the synthesis, and also to Messrs. May and Baker, Ltd., for gifts of 4 : 4′-dinitrostilbene. The microanalyses were carried out by Mr. D. **Skidmore**.

One of us (M.K.) is indebted to the University of Birmingham for a grant enabling him to carry out this work.

References p. 129.

SUMMARY

The relationship between the molecular structures of amines and the solubilities of their sulphates has been examined with the object of finding a better reagent than benzidine for the determination of sulphate. It has been established that the two aromatic rings must have a tendency to be coplanar and collinear, if the sulphate solubility is to be low. With the help of this theory, 4 : 4′-diaminotolane sulphate has been found to be less soluble than benzidine sulphate.

RÉSUMÉ

Le rapport entre les structures moléculaires des amines et les solubilités de leurs sulfates a été examiné, en vue de trouver un meilleur réactif que la benzidine pour le dosage de l'anion sulfurique. Les sulfates sont peu solubles si les 2 noyaux aromatiques peuvent avoir une configuration coplanaire et colinéaire. On a vérifié que le sulfate de 4.4′-diaminotolane est moins soluble que celui de benzidine.

ZUSAMMENFASSUNG

Man hat den Zusammenhang von der Molekülstruktur der Amine und der Löslichkeit deren Sulphate untersucht, um ein besseres Reagens als Benzidin für Sulphatbestimmungen zu finden. Es is festgestellt worden, dass die Sulphate schwer löslich sind, wenn die zwei aromatischen Kerne leicht in der selben Fläche und der selben Linie liegen können. Mittels dieser Theorie hat man gefunden. dass 4 : 4′-Diaminotolansulphat weniger löslich ist als Benzidinsulphat.

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UTILIZATION OF ION EXCHANGERS IN ANALYTICAL CHEMISTRY XXVI

APPLICATION OF THE ION-EXCHANGE METHOD TO SOLUTIONS CONTAINING OXIDANTS

by

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INTRODUCTION

In the first paper in this series[1] it was shown that cation-exchange resins can be used for an extremely simple and accurate determination of the total salt concentration in various electrolyte solutions. The principle is that the solution to be analyzed is passed through a column filled with a sulfonated resin in the free acid form. The cations are exchanged for an equivalent amount of hydrogen ions and, after washing the column with water, the liberated acids are titrated with standard alkali in the collected effluent. A large number of applications of this principle have been reported in earlier papers in this series and later by several other authors. The results have been summarized in a recent monograph[2].

In experiments with strongly oxidizing solutions complications occur. The ion exchanger is attacked and the ion-exchange method cannot be applied to the determination of total salt concentration. Examples are solutions containing bromate and iodate.

In other analytical separations certain anions are reduced only by cation exchangers in the free acid form but not by exchangers in the salt form. This fact has been used, *e.g.*, in the separation of alkali metals from chromate and molybdate by a cation exchanger in the ammonium form. Permanganate attacks the exchanger even if the exchanger is in the salt form[2].

The experiments referred to above have been performed with cation exchangers of sulfonated phenol-formaldehyde type (and in certain cases also with sulfonated coal). In recent years sulfonated hydrocarbon resins, *e.g.* sulfonated styrene-divinylbenzene resins, have been made available and as shown by BAUMAN, SKIDMORE AND OSMAN[3] these resins are more stable than earlier types of exchangers. The aim of the present investigation is to study the possibilities of using sulfonated hydrocarbon resins for analytical separations with solutions containing oxidants, which interfere when other resin types are used.

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EXPERIMENTAL PART

The ion-exchange column, which was of common construction[2], was filled with a cation-exchange resin of sulfonated hydrocarbon type (Dowex 50). The diameter and length of the resin bed were 9.8 mm and 130 mm. The resin (particle size 0.12—0.30 mm) was transformed into the free acid form by treatment with 4 *N* hydrochloric acid and subsequently washed with water until the effluent was neutral.

The alkalimetric determination of potassium bromate, potassium iodate, and potassium periodate according to the ion-exchange method was investigated in the first series of experiments. Solutions which had been standardized iodometrically were passed through the column and after washing with water the effluent was titrated with 0.1 *N* sodium hydroxide against methyl red. The sample solutions were about 0.05 *M* except in the case of potassium periodate where a lower concentration had to be used because of its low solubility. The time for filtration and washing was varied in different experiments. The washing was performed by means of 75 ml water.

The results presented in Table I show that good agreement has been obtained. The ion-exchange separation can be performed in ten minutes. Even if the time of contact between the solution and the resin is prolonged there is no reduction of the acid when this type of ion exchangers is utilized.

A second series of experiments were performed with solutions containing ammonium molybdate, potassium chromate, and potassium permanganate in order to determine if the hydrocarbon type of resin could be used for a transformation of the salts into the corresponding acids without any reduction of the anion. The molybdate solution had been standardized gravimetrically (lead molybdate), chromate iodometrically, and the permanganate by the oxalate method. The ion-exchange procedure was the same as described above. In the case of molybdate it was found necessary to use about 150 ml water to achieve a quantitative displacement of the liberated acid from the column. The effluents were analyzed according to the same methods as used in the standardization of the original solutions.

The results are reproduced in Table II. As seen from the table molybdate and chromate solutions are not reduced by the free acid form of the sulfonated hydrocarbon resin, whereas, even with this type of resin, a partial reduction of permanganate occurs.

Statens Tekniska Forskningsråd (The State Technical Research Council) has supported the research financially, which support is gratefully acknowledged.

TABLE I

ALKALIMETRIC TITRATION OF BROMATE, IODATE, AND PERIODATE

	Time for filtration and washing min	Added mmol	Found mmol	Relative error %
$KBrO_3$	10	2.509	2.509	±0.00
$KBrO_3$	10	2.509	2.509	±0.00
$KBrO_3$	30	2.509	2.504	-0.20
$KBrO_3$	30	2.509	2.506	-0.12
$KBrO_3$	60	2.465	2.460	-0.20
KIO_3	10	2.505	2.506	+0.04
KIO_3	30	2.505	2.503	-0.08
KIO_3	60	2.466	2.464	-0.08
KIO_3	60	2.466	2.465	-0.04
KIO_4	30	0.866	0.865	-0.12
KIO_4	30	1.757	1.756	-0.06
KIO_4	60	1.757	1.754	-0.17
KIO_4	60	1.757	1.756	-0.06

TABLE II

EXPERIMENTS WITH MOLYBDATE, CHROMATE, AND PERMANGANATE

	Time for filtration and washing min	Added mmol	Found mmol	Relative error %
$(NH_4)_2MoO_4$	10	2.920	2.916	−0.14
$(NH_4)_2MoO_4$	30	2.920	2.916	−0.14
$(NH_4)_2MoO_4$	60	2.920	2.917	−0.10
K_2CrO_4	10	2.500	2.500	±0.00
K_2CrO_4	10	2.500	2.502	+0.08
K_2CrO_4	30	2.500	2.499	−0.04
K_2CrO_4	30	2.500	2.499	−0.04
K_2CrO_4	60	2.500	2.497	−0.12
K_2CrO_4	60	2.500	2.499	−0.04
$KMnO_4$	10	0.975	0.948	−2.8
$KMnO_4$	18	0.975	0.945	−3.1
$KMnO_4$	18	0.975	0.939	−3.7
$KMnO_4$	35	0.975	0.916	−6.1
$KMnO_4$	83	0.975	0.854	−12.4

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SUMMARY

The free acid form of a cation-exchange resin of the sulfonated hydrocarbon type (Dowex 50) can be used for a quantitative liberation of the corresponding acids from salt solutions containing oxidants that are reduced by phenolic resins.
Positive results have been obtained with solutions containing bromate, iodate, periodate, molybdate, and chromate. With permanganate a partial reduction occurs which prevents the application of the ion-exchange method for quantitative separation of solutions containing permanganate.

RÉSUMÉ

La forme acide d'un échangeur de cations, résine du type hydrocarbure sulfoné (Dowex 50), peut être utilisée pour la séparation quantitative des anions d'une solution saline renfermant des oxydants, ces derniers étant réduits par des résines phénoliques. De bons résultats ont été obtenus avec des solutions de bromate, iodate, periodate, molybdate et chromate. Dans le cas du permanganate, il se produit une réduction partielle, la méthode proposée ne convient donc pas.

ZUSAMMENFASSUNG

Ein mit Wasserstoff-Ionen gesättigter Kationenaustauscher von sulfoniertem Kohlenwasserstoff-Typus (Dowex 50) kann auch bei der Anwesenheit von Oxidationsmitteln, welche durch Harze vom Phenol-Typus reduziert werden für die quantitative Überführung von Salzen in die entsprechenden Säuren verwendet werden. Positive Resultate wurden bei Lösungen von den folgenden Salzen erhalten: Bromat, Jodat, Perjodat, Molybdat und Chromat. Bei Permanganatlösungen tritt eine partielle Reduktion ein. Die Ionenaustausch-Methode kann deswegen bei Permanganatlösungen für quantitative Trennungen nicht verwendet werden.

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PAPER CHROMATOGRAPHY OF INORGANIC IONS

V. THE PREPARATION OF CARRIER-FREE ISOTOPES BY PAPER CHROMATOGRAPHY

by

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Carrier-free isotopes of natural and later of artificial radioactive elements have been prepared for about 30 years using various methods. (For an extensive treatise see 1). In a recent review[2] as well as in numerous articles [3, 4, 5, 7] GARRISON and co-workers describe the preparation of carrier free isotopes using conventional methods such as solvent extraction, coprecipitation, distillation, etc.

A number of separations employing ion-exchange chromatography have also been described and are reviewed by GARRISON above.

In this paper a number of preparations of carrier-free isotopes are described using paper chromatography as a method of separation, either alone or in conjunction with other methods. A brief account of this work was presented to the Journée de la Chromatographie sur papier (Paris, May 1952)[6].

Paper chromatography offers several advantages since the support of the carrier-free substance (*i.e.* the paper) can easily be ashed leaving only a negligible residue and thus losses due to adsorption to the vessels used for separation can be minimised. It was also possible to obtain more complete separations of carrier-free substances and the carriers than obtained by extraction methods (for example the separation of Rh and Fe). Finally in a number of purifications radioactive impurities were detected and identified, which would otherwise been overlooked. In the following pages the preparation of carrier-free ^{22}Na, ^{102}Rh, ^{103}Pd, ^{65}Zn and ^{233}U will be described in detail.

Separation of ^{22}Na tracer from Mg

^{22}Na may be obtained by bombardment of Mg with deutons $^{24}_{12}$Mg (d, α) $^{22}_{11}$Na. About 20 g of a sample of Mg bombarded with deutons were dissolved as the chloride and evaporated carefully to dryness and baked intensively over a bunsen flame. This hydrolyses the greater part of the $MgCl_2$ to MgO. After cooling, water is added to the residue and the insoluble MgO filtered off. As already observed by

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several workers [8, 9, 10] this oxide is completely inactive, all the activity going into solution.

The solution is now concentrated to a few ml and aliquots of *ca.* 0.2 ml are pipetted as a thin line 4 cm from the end of a sheet of Whatman No. 1 filter paper and developed by the ascending method for 10-20 hours with ethanol containing 20% water.

The chromatogram is then dried, a section 2 cm wide cut out and scanned with a Geiger counter to locate the activity (see Fig. 1). The band is then sprayed with $AgNO_3$ and exposed to sunlight yielding a dark brown band of AgCl where the $MgCl_2$ is situated.

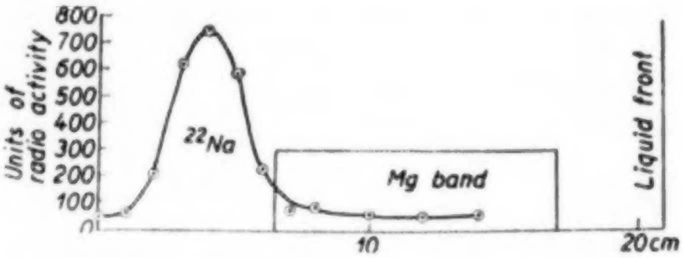

Fig. 1. Separation of ^{22}Na tracer from Mg. Solvent: ethanol 20% water.

The section of the sheet containing the activity *i.e.* between 2 and 6 cm from the starting line is cut out and extracted three times with double distilled water, filtered and evaporated dry. The residue so obtained was practically invisible.

Separation of ^{102}Rh tracer from Ru

$^{102}_{44}Ru$ (d,2n) $^{102}_{45}Rh$. No paper chromatographic separation of Rh and Ru was available and the method described by GILE, GARRISON AND HAMILTON[6,7] was tried, namely: fusion with Na_2O_2, volatilisation of RuO_4, precipitation of the Rh with $Fe(OH)_3$ and subsequent extraction of the Fe with ether and HCl.

We found that a source prepared in such a manner contained always a small brown residue due to unextracted Fe. By the use of paper chromatography it was however possible to remove also this residue.

The mixed $Fe(OH)_3$ and $Rh(OH)_3$ precipitate was dissolved in a few drops of HCl and placed on a band of paper. This was developed with a mixture of 20 ml of butanol and 10 ml conc. HCl. In this solvent Fe travels with the liquid front, while Rh remains in the R_F 0.1 region. The radioactive band is cut out and extracted repeatedly with small quantities of $2N$ HCl and evaporated to dryness on a watchglass.

A source so prepared had about the same residue as the acid used for extraction.

Separation of ^{103}Pd tracer from Rh

^{103}Pd (half life 17 days) was obtained by irradiating a foil of Rh with deutons. $^{103}_{45}$Rh (d, 2n) $^{103}_{46}$Pd. The irradiated Rh foil was heated numerous times (*ca.* 20 times) with 1 g lots of $NaHSO_4$ to red heat till all the Rh was dissolved. The Rh and Pd were precipitated from an aqueous solution from these fusions by addition of $Ni(NO_3)_2$ dimethylglyoxime and NH_4OH so as to coprecipitate the Pd with the Ni.

The precipitate was dissolved in aqua regia, evaporated to 1 ml, placed on several sheets of filter paper and each sheet developed with butanol shaken with *N* HCl.

The X-ray activity after 20 hours development is shown in Fig. 2.

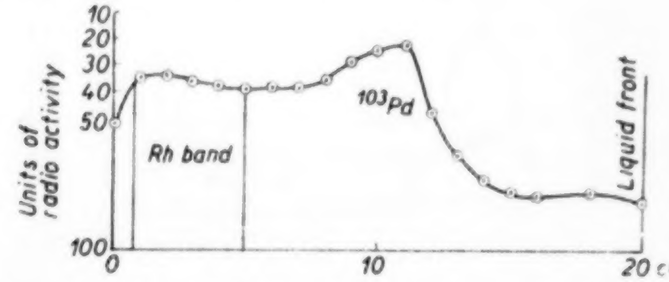

Fig. 2. Separation of ^{103}Pd from Rh. Solvent: butanol/*N* HCl.

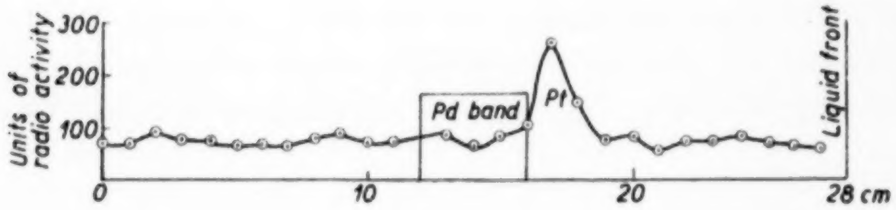

Fig. 3. Chromatogram of ^{103}Pd containing traces of active Pt.

The long comet and the second peak at the R_F 0.1 range suggest either another activity present or adsorption. As the source obtained was found to be of high radiochemical purity it appears that the trail is probably due to adsorption on the paper of some of the Pd. The peak of the band between 9 and 12 cm from the starting line, was cut out, ashed and dissolved in aqua regia and again evaporated.

The purification of another source of ^{103}Pd consisting of macro quantities (*ca.* 2 g) of Pd was attempted. A chromatogram developed with butanol/*N* HCl for 28 cm showed an activity near the visible band of Pd in the position of the Pt band as shown in Fig. 3. This activity, due to traces of Pt, could not be efficiently separated from the macro quantities of Pd by chromatographic methods as the two give adjacent spots in the solvents tried. Although such separations are quantitative for analytical purposes the overlapping activities are too large to produce a radiochemically pure source even after repeated chromatography.

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It was thus possible to detect the impurity of radioactive Pt, however without effecting a separation.

Identification of ^{60}Co in a source of ^{55}Fe

A sample (110 mg) of a ^{55}Fe source (obtained from Oak Ridge $^{54}_{26}$Fe (n, γ)$^{55}_{26}$Fe) was purified by precipitating with NH_4OH, dissolving the precipitate in HCl and chromatographing on several sheets of paper with acetone-HCl-water (90:5:5) Fe travels with the solvent front leaving behind an active band of R_F approx. 0.3. This band was eluted with 2*N* HNO_3 and rechromatographed with the same solvent, yielding a negligible residue on evaporation.

This activity was identified radiochemically and chromatographically by Michalowicz and Lederer to be ^{60}Co(II). A solvent extraction method for this separation was published by KENNY, MORTON AND SPRAGG[14].

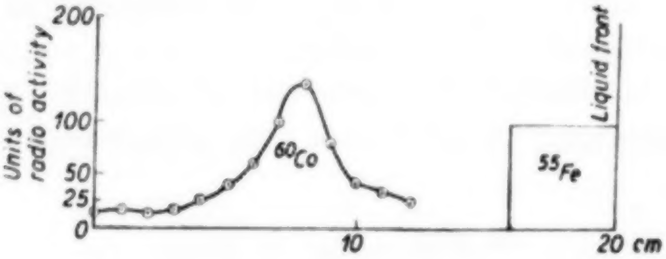

Fig. 4. Separation of ^{60}Co from a source of ^{55}Fe. Solvent: acetone, 5% HCl, 5% water.

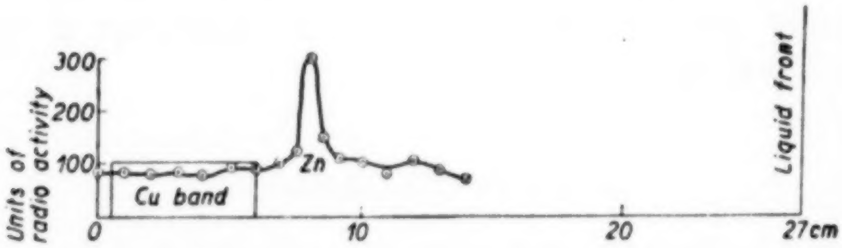

Fig. 5. Separation of ^{65}Zn from Cu. Solvent: butanol/*N* HCl.

Separation of $^{65}Z_n$ tracer from Cu

About 20 g of copper irradiated with deutons $^{65}_{29}$Cu(d,2n)$^{65}_{30}$Zn were dissolved in aqua regia and evaporated dry, taken up in dilute HCl and either the bulk of the Cu precipitated with H_2S as already described[12] or directly placed on sheets of filter paper and developed with butanol shaken with *N* HCl. After 20 hours the sheets are air dried and a green band of Cu is visible in the R_F 0.1 region.

The band of Zn can be detected with an X-ray counter and is about 2-3 cm ahead of the front of the Cu band as shown in Fig. 5.

The band of Zn can be cut out and ashed in a crucible leaving very little white residue.

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Separation of ^{233}U from ^{233}Pa

^{233}Pa was obtained by neutron irradiation of Th. Its decay (half life 27.4 days) produces ^{233}U

$$^{233}_{91}\text{Pa} \xrightarrow{\beta} {}^{233}_{92}\text{U}$$

A solution containing Pa and Th was obtained and the Pa, U and Th coprecipitated on $Fe(OH)_3$ with NH_4OH. The precipitate was redissolved in 2*N* HNO_3 and evaporated to a few drops. These were placed on paper strips and the beaker washed with a few more drops of dilute nitric acid and also placed on paper strips.

The paper strips employed for this separation were 4 cm wide and 20 cm long with a pointed end so as to concentrate the fast moving U. The chromatograms were developed downwards from a beaker holding ether containing 20% of conc. HNO_3[13], the whole being enclosed in a desiccator so as to minimise the volume for saturation of the atmosphere.

The tips of the chromatograms were cut off after the solvent had reached them and were extracted four times in a 1 ml beaker with 0.5 ml of 4% HNO_3.

Note added to proof

Preliminary co-precipitation of the Pd with Se and SO_2 greatly improves the separation of Pd-Rh on paper. The tail observed appears to be due to salting out by the large amounts of Rh present; it disappears if the preliminary treatment is carried out.

ACKNOWLEDGEMENTS

Thanks are due to Madame Joliot-Curie for kindly providing the facilities for this work, to M. M. Haissinsky and M. G. Bouissières for suggestions and advice, and to Mlle Y. Gable for technical assistance.

SUMMARY

Paper chromatography was employed for the separation of radioactive carrier-free isotopes from large amounts of inactive materials. The separations described are Na-Mg, Rh-Fe, Pd-Rh, Co-Fe, Zn-Cu and U-Pa.

RÉSUMÉ

La chromatographie sur papier a été utilisée pour la séparation des isotopes radioactifs de grandes quantités de substances inactives. Les séparations décrites concernent Na-Mg, Rh-Fe, Pd-Rh, Co-Fe, Zn-Cu et U-Pa.

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ZUSAMMENFASSUNG

Die Papierchromatographie wurde zur Trennung radioaktiver, trägerfreier Isotopen von einer grossen Menge inaktiven Materials verwendet. Es werden Trennungen für Na-Mg, Rh-Fe, Pd-Rh, Co-Fe, Zn-Cu und U-Pa beschrieben.

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LA SÉPARATION DU SCANDIUM, DU LANTHANE ET DE L'YTTRIUM

par

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Presque toutes les terres rares ont déjà été séparées l'une de l'autre, en utilisant l'échange ionique[1]. Comme le scandium se comporte chimiquement comme une terre rare, nous avons pensé étudier sa séparation du lanthane et de l'yttrium. Nous avons obtenu finalement une séparation satisfaisante en nous servant de l'acide citrique 5% à deux pH différents.

TECHNIQUE EXPÉRIMENTALE

On utilise la résine Amberlite IR 100 H de 80-120 mesh dans des colonnes de Pyrex, 0.7 cm de diamètre interne avec des longueurs de 8 cm pour les essais préliminaires jusqu'à 36.3 cm pour les séparations finales.

Le radioscandium ^{46}Sc, période 85 jours, provient de la pile de Harwell en Angleterre. Le radiolanthane ^{141}La, période 40 heures, et le radioyttrium ^{90}Y, période 62 heures, sont obtenus grâce à la pile de Châtillon. Ils sont tous livrés sous forme d'oxydes.

Comportement du scandium sur la colonne

On adsorbe 0.2 ml d'une solution de nitrate de scandium contenant 1 mg Sc_2O_3 par ml, sur une colonne de 36.3 cm, on lave avec 40 ml d'eau distillée et on élue avec de l'acide citrique à 5% de pH 2.8 à des vitesses entre 0.22 ml/min et 0.54 ml/min. La solution passe dans un petit serpentin enroulé autour d'un compteur G.M. et l'activité est mesurée toutes les cinq minutes.

On remarque que le maximum est atteint après 12.5 ml. Pour des vitesses supérieures à 0.45 ml/min, on a des irrégularités dans les courbes d'élution. On mesure le volume libre de la colonne en faisant écouler une solution concentrée de NH_4Cl et en mesurant le volume de liquide pour l'apparition des ions Cl^- à la base. On a trouvé une valeur reproductible de 8.2 ml.

D'autre part, on a calculé le volume libre d'après le poids et la densité de la

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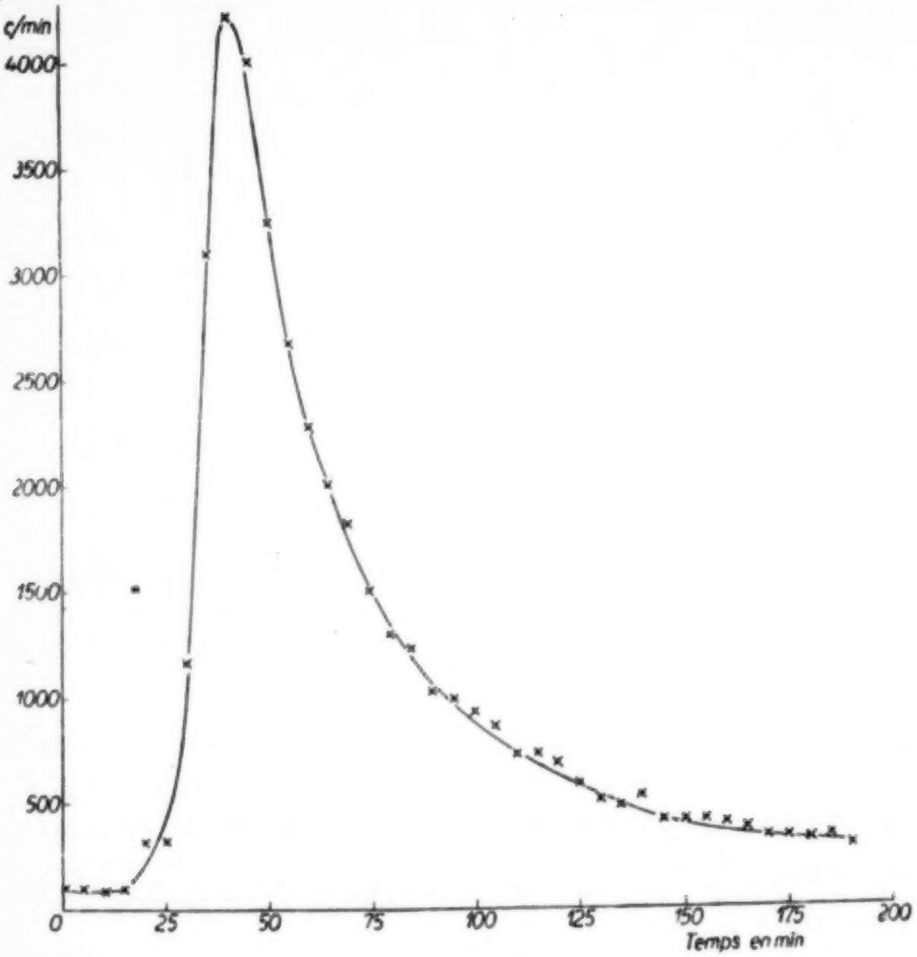

Fig. 1. Elution du scandium.
Vitesse d'élution 3.3 ml en 15 min.

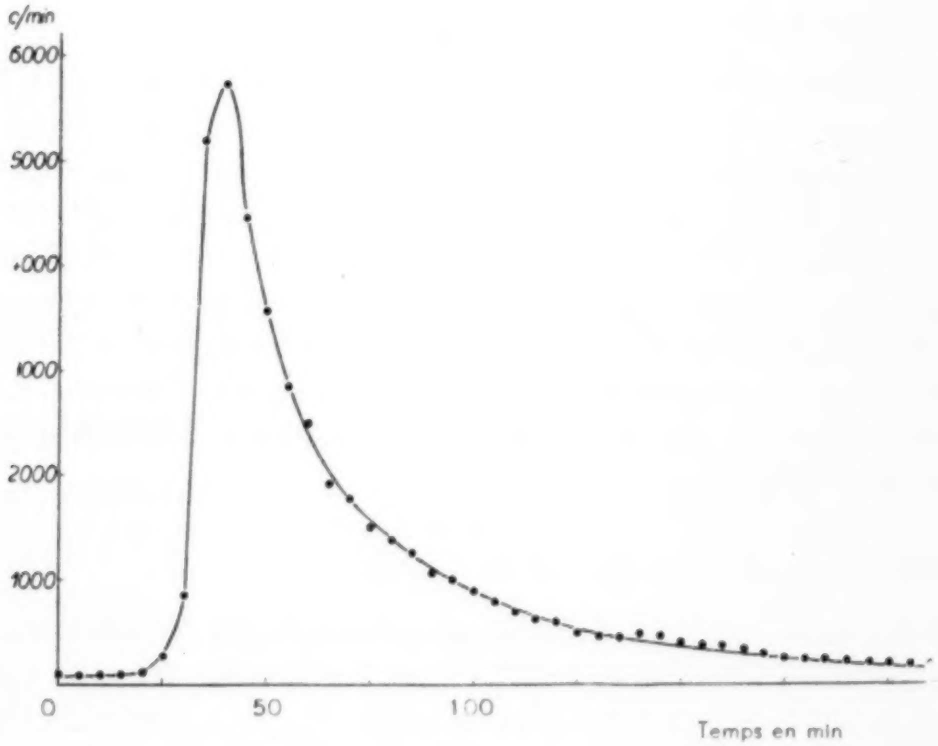

Fig. 2. Elution du scandium.
Vitesse d'élution 3.95 ml en 15 min.

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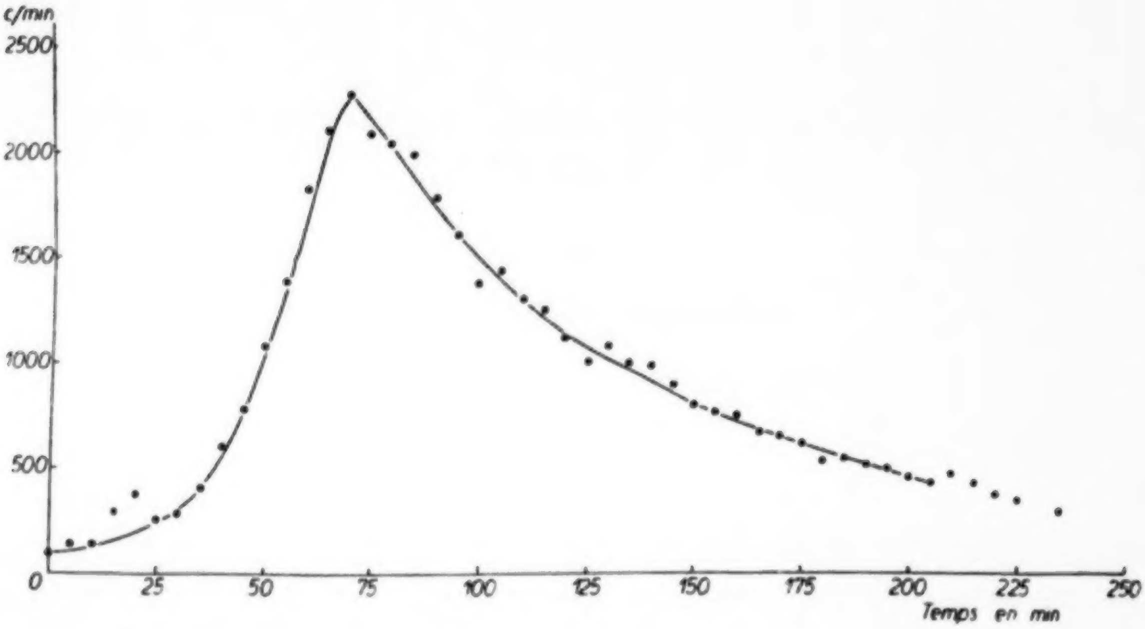

Fig. 3. Elution du scandium. Vitesse d'élution 5.3 ml en 15 min.

résine et on trouve 7.8 ml. On a aussi effectué des études à l'équilibre en agitant pendant 24 heures, 0.3 g de résine contenant ^{46}Sc comme indicateur, avec 25 ml d'une solution d'acide citrique à pH 2.8. Le coefficient de distribution $\frac{25}{0.3} \times \frac{\text{activité de la résine}}{\text{activité de la solution}}$ est environ 8.15. En agitant 0.3 g de la résine sous forme ammonium dans une solution d'acide citrique à 5% pH 2.8, contenant du radioscandium, on trouve une valeur d'environ 1.443.

Séparation du scandium et du lanthane

La colonne de longueur 36.3 cm contient 8.6756 g de l'Amberlite IR 100 H (pesée sec sous forme ammonium) mesh 80-120, de densité 1.407.

On adsorbe 2.5 ml d'une solution contenant un mélange des nitrates de scandium (1.0 mg Sc_2O_3) et de lanthane (3.7 mg La_2O_3), on lave, on élue avec l'acide citrique à 5% de pH 2.8. Des parties aliquotes de 4.3 ml sont recueillies toutes les vingt minutes avec un appareil automatique (Technicon Fractionater). Après quelques heures, on élève le pH à 3.2. Les parties aliquotes sont recueillies toutes les 30 minutes. On évapore 1 ml de chacune, on mesure l'activité. L'identité du lanthane est confirmée par la période de décroissance. Les résultats sont portés sur la courbe (Fig. 4).

Séparation du scandium et de l'yttrium

La même colonne sert pour la séparation scandium-yttrium. La solution adsorbée contient 4 mg Y_2O_3, 1 mg Sc_2O_3 sous forme de nitrates. Après lavage, on élue d'abord avec de l'acide citrique 5% (pH 2.8) on recueille les parties aliquotes

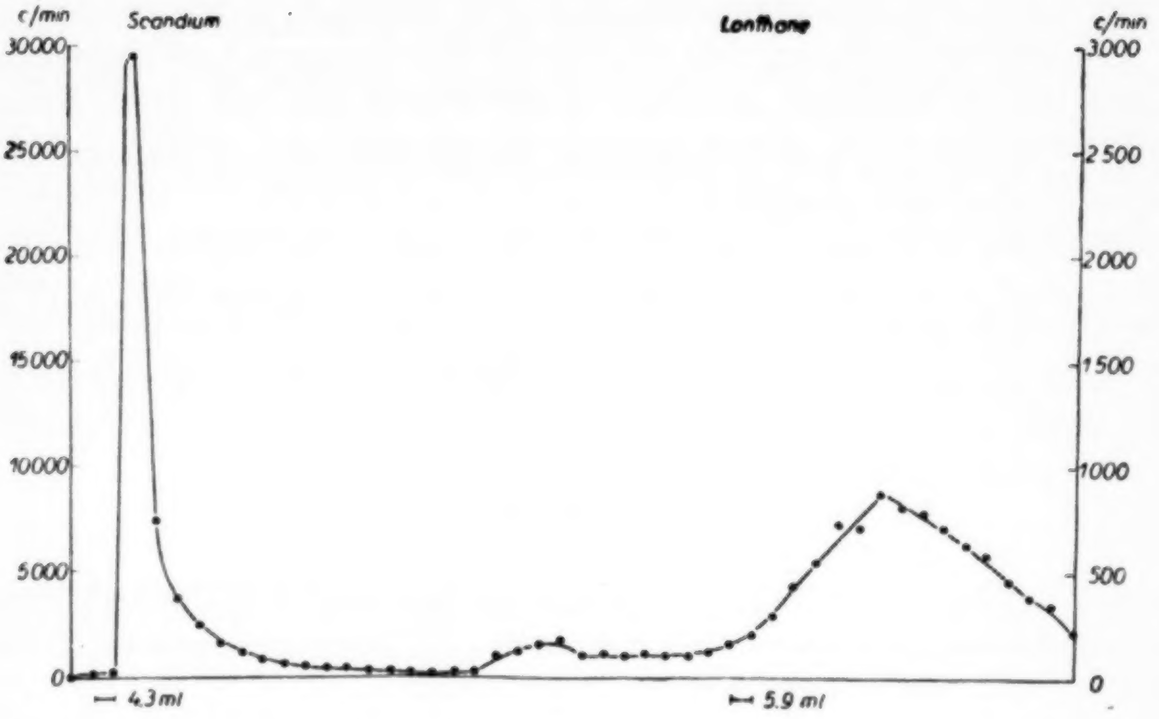

Fig. 4. Séparation du scandium et du lanthane.

de 4.35 ml toutes les 20 minutes, on fait remonter le pH à 3.2 et on recueille les parties aliquotes de 5.75 ml toutes les 30 minutes.

On confirme l'identité de l'yttrium par sa période. Les résultats sont portés sur la courbe.

DISCUSSION

Les études sur la vitesse d'élution montrent que les courbes d'élution sont beaucoup plus étalées pour un écoulement rapide. Les vitesses lentes, 0.22 ml/min à 0.26 ml/min, donnent des sommets plus prononcés. A cause de ce fait, nous avons toujours choisi les vitesses lentes pour obtenir une séparation du scandium.

Nos résultats, pour l'équilibre entre la résine et une solution d'acide citrique à 5% (pH 2.8) contenant des ions scandium, montrent qu'il y a un effet d'hystérésis dans l'adsorption.

Les réactions qui jouent dans le cas de l'adsorption d'une solution de citrate sont:

1 l'échange $Sc^{+3} + 3\,NH_4R \rightleftarrows ScR_3 + 3\,NH_4^+$;

2 la formation des complexes:

$$Sc^{+3} + n\,H_x\,Cit^{(x-3)} \rightleftarrows Sc(H_x\,Cit)_n^{3+n(x-3)}$$

NH_4R est la résine sous forme ammonium, $H_x\,Cit^{(x-3)}$ est un ion citrique, $Sc\,(H_x Cit)_n^{3+n(x-3)}$ est le complexe citrique du scandium, n et x sont des constantes. Le coefficient de distribution

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$$K_d = \frac{(\mathrm{ScR})}{\mathrm{Sc}\ (\mathrm{H}_x\mathrm{Cit})_n{}^{3+(x-3)}} = \frac{K_{\text{échange}}}{K_{\text{complexe}}} \quad \frac{(\mathrm{NH_4R})^3}{(\mathrm{NH_4^+})} \quad \frac{1}{(\mathrm{H}_x\mathrm{Cit}^{x-3})^n}$$

où $K_{\text{échange}}$ et K_{complexe} sont les constantes d'équilibre pour les réactions d'échange et de formation des complexes.

En l'absence de facteurs perturbateurs, la constante d'équilibre pour l'échange $\mathrm{Sc^{+3} + 3\ NH_4R \rightarrow ScR_3 + 3\ NH_4R}$ et pour la réaction inverse $\mathrm{ScR + 3NH_4^+ \rightarrow Sc^{+3} + 3\ NH_4R}$ devrait être la même.

En présence des tels effets, le coefficient de distribution changera avec le sens dans lequel on approche de l'équilibre.

Par exemple, pour les cas des échanges

$$\mathrm{Ba^{+2} + 2\ NaR \rightleftarrows BaR_2 + 2\ Na^+}\ \text{et}$$
$$\mathrm{La^{+3} + 3\ NaR \rightleftarrows LaR_3 + 3\ Na^+}$$

BOYD, SCHUBERT ET ADAMSON ont trouvé qu'elles étaient différentes[2]. Quelques études de SCHUBERT confirment l'existence de ce phénomène appelé hystérésis et il l'attribue aux effets stériques[3].

L'hystérésis est mesuré par le rapport entre les constantes d'équilibre. Pour notre cas, on a le rapport

$$\frac{K_{d1}}{K_{d2}} = \frac{8.15}{1.44} = \frac{\text{coefficient avec Sc sur la résine}}{\text{coefficient avec Sc en solution}}.$$

Nous soulignons l'importance de ce phénomène quand on veut appliquer la théorie des plateaux de TOMPKINS ET MAYER pour calculer la courbe d'élution à partir des résultats obtenus à l'équilibre[4].

Le maximum de concentration du scandium dans la solution élue est, d'après cette théorie, donné par

$F_{\max} = C = K_d \times \frac{m}{v}$ ou v = volume libre dans la colonne, m = masse de

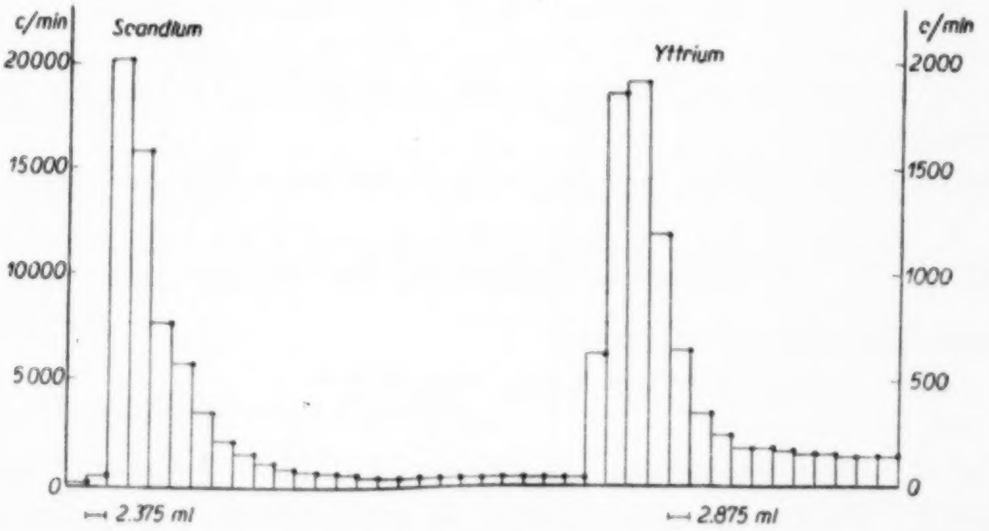

Fig. 5. Séparation du scandium et de l'yttrium.

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résine, C = rapport des fractions de la masse du scandium dans la résine et dans la solution à l'équilibre.

A priori, on ne peut pas décider quelle valeur du coefficient de distribution, K_{d1} ou K_{d2}, il faut substituer ici. Nous avons trouvé une bonne concordance avec l'expérience en prenant $K_d = 1.44$, c'est à dire, la valeur du coefficient de distribution obtenu pour le cas où le scandium se trouve initialement en solution.

Je remercie Mme I. JOLIOT-CURIE pour l'intérêt qu'elle a bien voulu y porter. Je remercie également Mlle I. KADOMTZEFF ET M. R. BOUCHEZ pour leurs nombreux conseils.

RÉSUMÉ

On a étudié le comportement du scandium sur une colonne de résine et effectué une séparation efficace du scandium, du lanthane et de l'yttrium en se servant de l'acide citrique à pH différents. Le phénomène d'hystérésis qui accompagne l'adsorption du scandium et son importance pour des calculs, basés sur la théorie des plateaux, sont discutés.

SUMMARY

The behaviour of scandium on a resin column has been studied and an efficient separation of scandium, lanthanum and yttrium has been effected using citric acid at different pH's. The hysteresis phenomenon which accompanies the adsorption of scandium and its importance for calculations, based on the theory of levels, are discussed.

ZUSAMMENFASSUNG

Es wurde das Verhalten des Scandiums in einer Harzkolonne untersucht und die wirksame Trennung des Scandiums, Lanthans und des Yttriums unter Benutzung von Zitronensäure bei verschiedenem pH bewerkstelligt. Das hysteretische Phänomen, das die Adsorption des Scandiums begleitet und seine Wichtigkeit für Rechnungen, die sich auf die Theorie der Fraktionierböden gründen werden besprochen.

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4:4'-DIAMINOTOLANE AS A REAGENT FOR THE TITRIMETRIC DETERMINATION OF SULPHATE

by

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In a recent communication to this Journal[1] we advanced a tentative theory relating the insolubility of certain amine sulphates with their structure. By application of this theory we predicted that the compound 4:4'-diaminotolane should form a more sparingly soluble sulphate than benzidine, and confirmed this experimentally. This was the first time that an amine sulphate less soluble than benzidine sulphate had been recorded. We have since examined 4:4'-diaminotolane as a reagent for the determination of sulphate, and the present paper describes the results of the investigation. 4:4'-Diaminotolane can be recommended in place of benzidine for the determination of sulphate; as would be expected from the greater insolubility of the sulphate (0.059 g/l at 25°C, *cf.* benzidine sulphate, 0.098 g/l at 25°C) the results are more accurate. Moreover, it was found that the interference of other ions was much less marked.

Effect of excess reagent

Experiments in which different quantities of reagent were used to effect precipitation showed that a four and a half times excess was the most suitable. With smaller quantities of reagent results were slightly low; larger quantities of reagent had no deleterious effect. In each case the final volume of the solution was 100 ml and the precipitate was allowed to stand overnight. The precipitations were carried out at pH 4.

Variation of standing time

Satisfactory results were obtained between pH 3 and 4 when the precipitate was allowed to stand for 15 minutes after addition of the reagent, but results were slightly low at acidities between pH 2 and 3 with the same standing time. When the standing time was increased to 30 minutes, satisfactory results were obtained between pH 2 and 4.

Effect of acidity

Good results were obtained between pH 2 and 4 on 25 mg quantities of sulphate; at lower pH values recoveries were incomplete, even when the standing time was increased to 12 hours. A selection of results is given in Table I.

TABLE I

THE EFFECT OF ACIDITY ON THE DETERMINATION OF SULPHATE WITH 4:4′-DIAMINOTOLANE

(25.33 mg of SO_4^{-2} present)

pH	SO_4^{-2} found (mg)		
3.4	25.34	25.31	25.37
2.0	25.31	25.32	
1.5	25.04	25.07	

Sensitivity

The method gave good results for quantities of sulphate greater than 10 mg. Below this, the results were slightly low, but could be tolerated for certain types of analysis. Typical results for a range of sulphate values are included in Table II. Amounts of sulphate greater than 25 mg were not examined, since it is in the lower concentrations that the benzidine method fails. It would be expected, however, that 4:4′-diaminotolane would give more accurate results than benzidine at higher levels. For quantities of 15 mg or more, 0.05 *N* alkali was used for the titration of the precipitate; for smaller quantities, 0.02 *N* alkali was used. The volume of the reagent solution was decreased proportionately.

These results are better than those quoted for benzidine[2]. In the determination of 12 mg of sulphate ion with benzidine, errors of 3-4% are obtained, and a standing time of 3-4 hours is necessary. In the determination of 10 mg of sulphate, the error is 6%. The corresponding errors obtained with 4:4′-diaminotolane are 0.7% using a standing time of only thirty minutes.

TABLE II

DETERMINATION OF DIFFERENT AMOUNTS OF SULPHATE WITH 4:4′-DIAMINOTOLANE (pH 3)

SO_4^{-2} taken (mg)	SO_4^{-2} found (mg)		Reagent volume (ml)
15.20	15.18	15.16	60
10.13	10.06	10.08	50
7.39	7.33	7.34	30
5.28	5.19	5.23	20
4.22	4.06	4.08	16
2.11	2.09	2.08	10

Effect of foreign ions

As with benzidine, phosphate and chromate interfered in the determination. However, since trivalent chromium was without effect, the chromate ion could easily be reduced without affecting the subsequent determination of sulphate. Aluminium interfered, but its effect could be overcome by the addition of tartaric acid.

Ferric iron gave an orange-red precipitate with the reagent, but on filtration much of this appeared to pass through in colloidal form and results were only slightly low. The colour of the precipitate faded during the titration, and the end-point could be detected without difficulty. Copper gave a yellow-green coloration and eventually a yellow precipitate, but this did not affect the results.

Nitrate, perchlorate, chromium, zinc, calcium and magnesium ions did not interfere. The lack of interference from nitrate and magnesium is another advantage over the benzidine method[2,3].

In each case 100 mg of the foreign ion were present and all determinations were carried out at pH 3. Results are listed in Table III.

TABLE III

DETERMINATION OF SULPHATE WITH 4:4'-DIAMINOTOLANE, IN PRESENCE OF VARIOUS IONS (10.13 mg of SO_4^{-2} present)

Ion	SO_4^{-2} found (mg)
NO_3^-	10.08
PO_4^{-3}	26.26
ClO_4^-	10.08
CrO_4^{-2}	3.81
Cu^{+2}	10.15
Al^{+3}	1.74
Al^{+3} (+ tartrate)	10.04
Cr^{+3}	10.08
Fe^{+3}	9.91
Zn^{+2}	10.06
Ca^{+2}	10.10
Mg^{+2}	10.12

EXPERIMENTAL

Reagent. A saturated solution of 4:4'-diaminotolane hydrochloride in water. 1 g of 4:4'-diaminotolane was dissolved in 5 ml of acetone and concentrated hydrochloric acid was added dropwise until precipitation of the hydrochloride was complete. This was filtered at the pump and dissolved in 375 ml of water. The solution was filtered, and a few drops of acetone or 1 *N* hydrochloric acid

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added until clear. The reagent should be prepared fresh for each series of determinations, although it was found that it did not deteriorate after standing for 24 hours. The reagent should not be heated, otherwise the 4:4′-diaminotolane may be converted in part to 4:4′-diaminodesoxybenzoin.

Procedure. The reagent (90 ml for each 25 mg of sulphate) was added to the sulphate solution in a 100 ml beaker. A little paper pulp was added, the volume made up with water to 100 ml and the pH adjusted to the required value by dropwise addition of 1 *N* hydrochloric acid. After 30 minutes, the mixture was filtered through a pulp pad using water as the transferring liquid. The precipitate was washed with water (*ca.* 12-15 ml) until the washings were chloride-free. The pad was transferred to a 100 ml beaker, the volume adjusted to 30-40 ml with water, 5 drops of 0.1% phenolphthalein indicator were added and the boiling mixture was titrated with standard sodium hydroxide solution to the first appearance of a pink colour.

A determination may be completed in about 45 minutes.

SUMMARY

4:4′-Diaminotolane is recommended instead of benzidine as a reagent for the titrimetric determination of sulphate. The method cannot be carried out in the presence of phosphate or chromate ions, but nitrate, perchlorate, cupric, chromic, ferric, zinc, calcium and magnesium ions are without effect. Interference due to aluminium ions can be avoided by the addition of tartaric acid. The experimental procedure is described.

RÉSUMÉ

Le 4:4′-diaminotolane est recommandé comme réactif pour la détermination titrimétrique des sulfates. La détermination n'est pas possible en présence de phosphates ou de chromates, mais les nitrates, les perchlorates et les ions du cuivre, chrome, fer(III), zinc, calcium et magnésium sont sans influence. En présence de l'acide tartrique, l'aluminium ne gêne pas. Le mode opératoire est décrit.

ZUSAMMENFASSUNG

4:4′-Diaminotolan wird anstatt Benzidin als Reagens für die massanalytische Bestimmung von Sulphat empfohlen. In Gegenwart von Phosphaten und Chromaten ist die Bestimmung unmöglich, aber Nitrat-, Perchlorat-, Kupfer-, Chrom-, Eisen-(III)-, Zink-, Calcium- und Magnesiumionen sind ohne Einfluss. Die störende Wirkung von Aluminium kann man mit Weinsäure vermeiden. Das experimentale Verfahren wird beschrieben.

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FLAME PHOTOMETRIC DETERMINATION OF SODIUM AND POTASSIUM IN SOME BIOLOGICAL FLUIDS

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INTRODUCTION

The rapid and accurate determination of sodium and potassium in body fluids such as blood serum and urine has proved to be of increasing importance for clinical examinations. The classical chemical methods of separation and determination are particularly laborious and time-consuming, and, especially for potassium, not very accurate. In clinical practice the gravimetric method of sodium determination is carried out as a rule, this consisting of the precipitation of sodium as sodium uranyl zinc acetate[7,16], while for potassium the cobalt nitrite method is usually applied[6,11].

The present development of the spectrochemical method of analysis (in which the emission spectrum of an element, heated to a high temperature, is measured), has enabled us to carry out the determination of sodium and potassium in an extremely rapid and simple way. The method, at present generally referred to as flame photometry, is based on the principle that every element in the form of glowing vapour emits a characteristic line spectrum. The substance under test is brought into the flame, which causes a dissociation of the composing elements. Then these elements, the atoms of which are excited, emit light in turn. As the intensity of the spectral lines is a function of the number of atoms excited and thus of the content of a certain element in the solution under test, it is possible, by comparison with a standard, to determine the concentration of a given element in the sample to be investigated.

To carry out an analysis, the material under test (in solution) is atomized with compressed air into a colourless flame. Then the light of the wave-length suitable for measuring is isolated by means of filters. The intensity of the spectral lines is measured with a photosensitive receptor. The measurements are carried out by comparing the intensity of the emission spectrum with that of standard solutions of known concentration.

The rapid and simple technique of flame photometric analysis is greatly preferable to the troublesome and time-consuming chemical methods of determination, especially in serial investigations.

However, in order to obtain accurate and reproducible values with the flame photometric method, there should be an empirical investigation of the influence of various admixtures in the solution under analysis on the intensity of the spectral line to be measured. This effect of other ions and admixtures on the emission of the element to be determined constitutes the main source of error in flame photometric determinations carried out without precautions.

APPARATUS

In our investigation we used the LANGE flame photometer[13], which comparatively simple apparatus is already in use in various clinical laboratories. The instrument consists of the following parts:

(1) Needle valves, for the regulation of a constant pressure of air and gas.
(2) Manometers, indicating the working pressure of gas and compressed air.
(3) Atomizer.
(4) Flame photometer (burner, optics, selenium cell).
(5) Galvanometer.

Gas and air supply and regulation of pressure

Various gases may be used for burning in the flame, such as the following combinations: acetylene/air, butane/air and coal-gas/air. In our investigation we used coal-gas/air, because we did not consider the use of acetylene gas to be free from danger, and usually the carrying out of flame photometric analyses in serial investigations is entrusted to less skilled personnel.

Working under fixed conditions of gas and air pressure is necessary for a reproducible and constant flame emission. Therefore the coal-gas, obtained directly from the municipal gas-main, is led via a needle valve and an automatic gas pressure regulator into the burner. Slight variations in gas pressure, if present, could be eliminated completely by means of a number of rubber balloons placed in the gas tubing before the needle valve, the expansion space of which served as a buffer in the gas supply system. By means of this combination of rubber balloons, automatic pressure regulator and needle valve, it was possible to obtain the desired working pressure of the coal-gas and to maintain it completely at a constant level. The air used for the flame and also for the atomization of the solution under analysis was supplied from cylinders containing compressed air. The air pressure was kept quite steady by means of a combination of a 2-stage reducing valve, a regulation valve (serving at the same time as air filter), and a needle valve.

The pressure of the coal-gas as well as that of the air is measured with so-called flow manometers. With these, differences of pressure in the supply tubings are measured, so that possible obstructions and changes of resistance in the tubing, atomizer or burner do not affect the results; thus we are ensured of a constant flow of gases to the flame.

Atomizer

The present construction of the now generally used inhalation atomizers is such that cleansing after every analysis is no longer necessary, so that the apparatus may be used continuously.

Fig. 1 shows the atomizer used, combined with the burner.

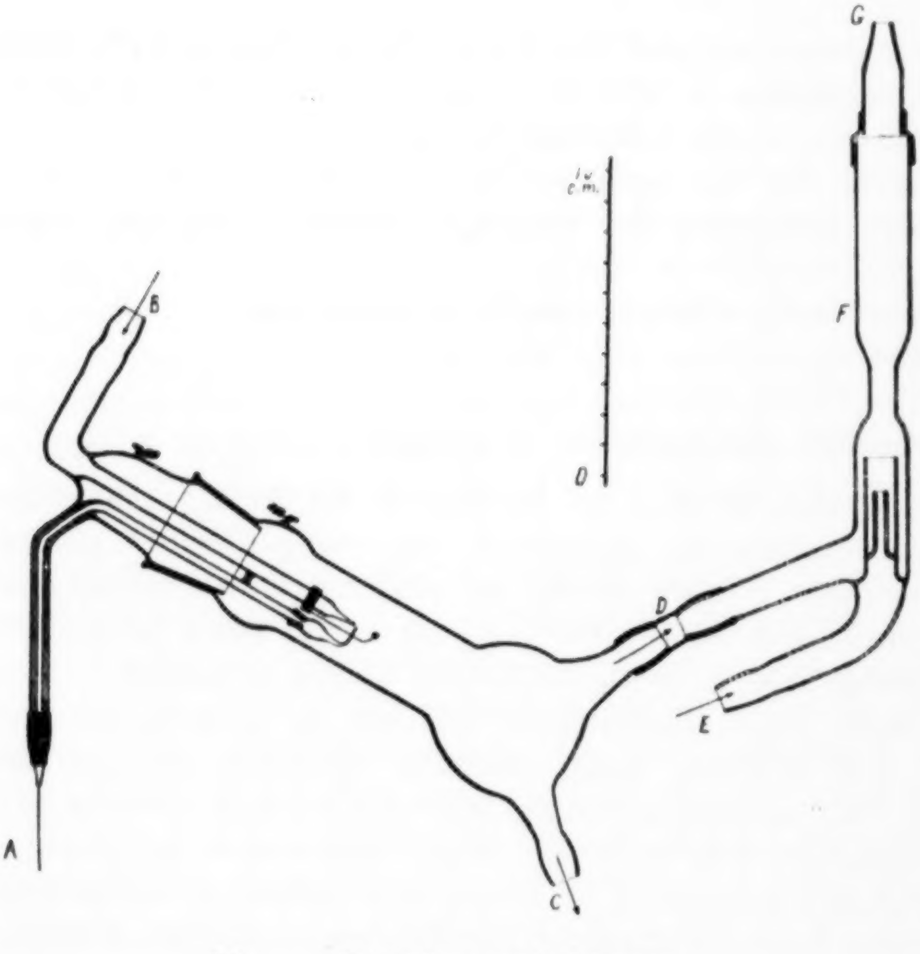


Fig. 1. Atomizer and burner.

The compressed air is introduced at B into the atomizer. Thus a negative pressure arises, and the solution to be analysed is sucked at A into the vertical capillary tube and blown into a fine spray at the narrowed orifice in the atomizer. In order to obtain a reproducible and constant flame emission the formation of bigger droplets of fluid must be avoided as much as possible; only the finest mist, the water and salt particles of which can evaporate sufficiently rapidly in the flame, can be used for the emission of light. By placing a small metal bulb as a disperser in the expansion chamber before the outlets of the capillaries, the fluid can be reduced to the desired fine mist; moreover this increased the atomizing effect considerably. As the mist has to cover a comparatively great distance before reaching the flame, the bigger droplets of fluid precipitate against the side and back walls of the expansion chamber; they flow off at C. Here the atomizer is closed with a U-tube, so that the pressure in the atomizer remains always constant.

Burner and flame

The construction of the burner (Fig. 1) guarantees a close mixture of the flame gases, which is a necessary condition for a constant emission. The flame is fed with coal-gas, which is introduced at E, and with the air, which enters the burner at D via the atomizer, carrying with it the solution under test as a fine mist. The burners used for the various gases (acetylene, propane, butane or coal-gas), differ in the diameter of their outflow capillaries, while there are also differences in the diameters of the burner heads. For the coal-gas burner these figures are 2 mm and 6.5 mm, respectively.

The outflow capillary in the burner is protected by a glass mantle in order to prevent the precipitation of the mist against this capillary. This might lead to deposition of fine crystals in the capillary, possibly resulting in complete or partial obstruction, with an unfavourable influence on a regular gas flow.

The use of the flame offers advantages in comparison with the spark or the light arc for quantitative intensity determinations of emission spectra. The most striking advantages of the flame method are the completely constant and reproducible light emission, the spectrum of the flame which shows relatively few lines, and the simple and reliable way in which the solution under analysis can be carried into the flame. However, owing to the comparatively low temperature, the use of the flame is limited to elements with spectral lines of low excitation-potentials (1—4 eV). It is fortunate that the majority of the biologically important cations belong to this small group of elements.

Measuring apparatus

A photocell is used for the measurement of the intensity of the light emitted by the flame. The photoelectric current produced in the photocell is measured with a galvanometer.

The determination of a single cation in solution can be carried out in a simple way by using a series of standard solutions and determining the content by interpolation of the galvanometer values; as interference by other spectral lines does not occur in this case, a filter between flame and photocell would also be superfluous.

As in practice we are dealing with mixtures of ions, it is necessary to select the spectral lines by means of optic filters. In general the following filters can be used for the selection of the light emitted: colour filters (gelatin, liquid and glass filters), the dispersion filter of CHRISTIANSEN[8], a monochromator or an interference filter. As it is of importance in the quantitative spectral analysis to select a single spectral line, the filters used must be as selective as possible and they should possess a maximal transmission for this particular spectral line.

The ordinary colour filters have a great area of transmission and, on account of their slight selectivity, they are less suitable for flame photometric analysis. Boon described in his academical thesis[5] the use of a Christiansen filter. This filter acts as a good monochromator in the yellow and blue areas of the spectrum. A disadvantage of this filter system is the rather complicated arrangement of thermostat and lenses.

A monochromator is frequently used in flame photometric analysis. It is as a rule to be recommended in those cases in which the spectral lines lie very close together and/or when they are very weak, so that isolation by filters cannot take place completely. Monochromator optics are comparatively costly and rather complicated; moreover there is soon a limit to the intensity of the light. Use of filters with a larger effective surface guarantees a spectrum of considerably greater light intensity than when a monochromator is used. Admixtures of the fluid under test, however, may exert an influence on the determination, if these substances emit light of wavelengths situated in the neighbourhood of the wave-lengths of the light emitted by the element to be determined. However, in the

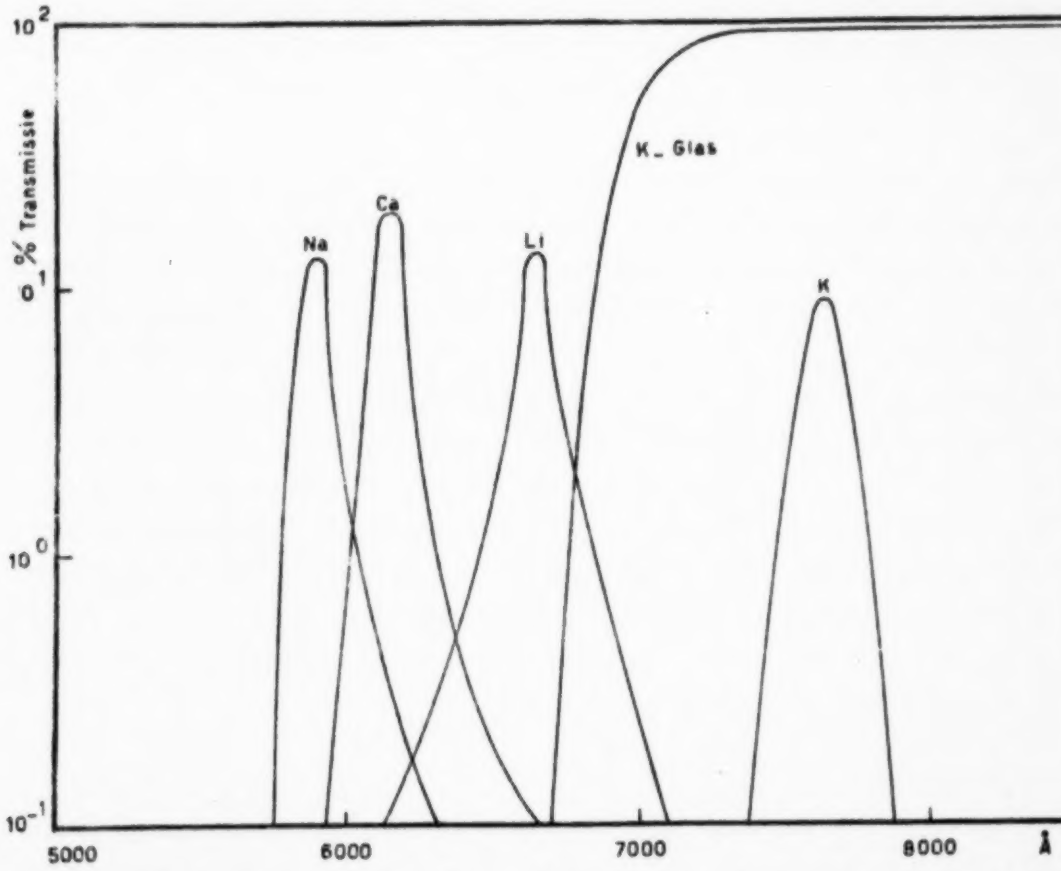


Fig. 2. Transmission curves for the sodium, potassium, calcium and lithium interference filters and for the potassium red filter RG8.

problems of flame photometry raised here, the place in the spectrum of the spectral lines to be measured is not so important that the use of a monochromator is absolutely necessary. Therefore we prefer filters, because, on account of the greater effective surface, their light intensity is greater. Thus stronger photo currents become available than with the use of a monochromator.

For the isolation of the sodium doublet 5890/5896 A we used the SCHOTT interference filter FV0589. Interference filters are pre-eminently suitable for flame photometric analysis: they approach the monochromator in selectivity, but they are far simpler and cheaper. They possess on an average a maximum transmission of 15—30%[10]. The wave-length of maximum transmission of the sodium interference filter used by us lies at 5900 A, the maximum transmission is 17% (Fig. 2).

For the determination of potassium we used a glass filter (SCHOTT RG8 red filter). The potassium radiation 7665/7699 A to be measured is well transmitted by this filter (maximum transmission 96%), the sodium and calcium lines are practically completely stopped. The filter was more satisfactory than the potassium interference filter we had at our disposal, as the maximum transmission of the latter was only 9%, so that the potassium determinations carried out with this filter were considerably less sensitive. The transmission curves of these filters are also reproduced in Fig. 2.

A selenium photocell was used as photosensitive receptor. Its maximum sensitivity lies at about 5600 A, in the vicinity of the sodium double-line. The sensitivity is considerably smaller in the area of the potassium lines 7665/7699 A (Fig. 3).

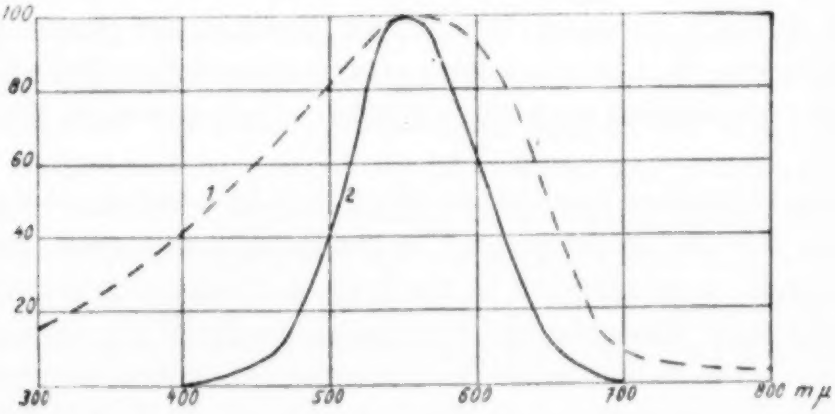


Fig. 3. Spectral sensitivity of selenium element (1) and mean eye sensitivity (2)

The sensitivity of the potassium determination may be increased by using photocells with a greater sensitivity in the red spectral region (*e.g.* caesium cells). However, these cells have a considerable internal resistance and yield such a weak current that this must be amplified. The potassium determination is sufficiently sensitive when the selenium element is combined with the RG8 red filter and a sensitive galvanometer, so that we retained this photo element for the potassium determination. Exchange of photo element and caesium cell for simultaneous sodium and potassium determination is superfluous, as is also amplification of the current.

The current from the selenium element is fed directly on to the galvanometer. The Multiflex galvanometer, originally indicated for this use, was replaced by a more sensitive type, the A 75 of KIPP Ltd., Delft (maximum sensitivity 5.10^{-10} A/mm).

EXPERIMENTAL PART

The method of choice to obtain reliable data would be the use of standard solutions, with a composition agreeing completely with that of the solutions under investigation. However, in practice this appears to be impossible, as in most cases we are dealing with complicated mixtures with ionic relationships varying considerably mutually. If we accept a difference in composition between standard solution and solution to be analysed, we must know the influence of the various admixtures in the test solution on the intensity of the spectral line to be measured, in order to obtain accurate and reproducible data. Then for each of the admixtures present a possible effect on the sodium and potassium determination can be corrected.

The causes of the many interference effects which may occur in the analysis and which are also mentioned in most of the publications on flame photometry, constitute an in general highly confusing picture, the more so as numerous factors play a rôle in it.

Various methods may be applied for the correction of the disturbances (which form the most difficult problem for correct quantitative flame photometry), because, as said before, it is impossible to prepare standard solutions which agree in all respects in composition with the solution to be examined. We mention the following:

(a) The internal standard method, in which, by the addition of a given amount of lithium (which element is not present in the fluids under test), the ratio of the sodium or potassium concentration to the known lithium concentration is determined photoelectrically. Disturbances impossible to check (*e.g.* in the atomization) may be compensated in this manner, as the same influences manifest themselves with respect to the internal standard element lithium. To this end the apparatus must be equipped with two photocells and double optics (BERRY *et al.*[4], BERNSTEIN[3], PERKIN-ELMER[15], SPENCER *et al.*[18]).

(b) The semi-internal standard method, in which the normal simple optic is used. A given amount of lithium salt is again added to the solution under investigation. Together with the sodium/potassium determination a flame photometric lithium determination is carried out by measurement against two simple lithium standard solutions. The effects that should occur may easily be determined in this way, and the sodium and potassium determinations can be corrected.

(c) Addition of so-called radiation buffers to standard solution and test solution. This addition consists of an excess of the interfering element, so that the slight concentrations of this element in the original fluid are negligible (DUFFENDACK[9], WEST *et al.*[22], WEICHSELBAUM[21]).

(d) The direct addition method, in which given amounts of sodium or potassium are added to the solution under analysis; the original quantity of sodium or potassium may be determined from the increase of light intensity by extrapolation in a constructed graph (ADDINK AND DE GROOT[1], OSBORN AND JOHNS[14]).

The disturbances, which are observed as an influence on the galvanometer deflection and which originate in a difference in composition of standard solution and solution under investigation, may have various causes. The most important of them are:

(1) Influence on the atomization and mist formation.
(2) Disturbance due to insufficient selectivity of the filters.
(3) Mutual interference in the flame.

When various flame gases are used (acetylene, propane or coal-gas), the disturbances occurring in the sodium and potassium determination will be very different on account of the different temperatures. Therefore the disturbances must be examined for each of these gases separately.

In general, standard curves are used in the analysis. In these graphs the sodium or potassium contents are plotted on the abscissa, the galvanometer deflection on the ordinate. The content may be read off directly by means of a graph so constructed. Permanent use of such curves without correction would, however, only be feasible if all circumstances on which the experiment is dependent, were always constant and reproducible. As it is, however, impossible to realize completely the conditions for a regular gas and air supply, for a constantly working atomizer and burner and for a regularly functioning photo element — to mention only some items — it is always necessary to check the course of the curve and, if necessary, to correct it by means of the standard solution with which the assaying has also taken place. Thus a direct advantage of the use of the curves is lost, especially in those cases in which incidental changes in the experimental conditions may easily occur.

For this reason we preferred the method of interpolation as a method of measurement. Together with the measurement of an unknown solution the galvanometer deflections of two standard solutions are determined, one with a higher and the other with a lower concentration than the unknown solution. The content of the solution under test is then found by interpolation. The standard solutions and the measuring capacity of the galvanometer are always selected in such a way that we may speak of a linear measuring range, so that interpolation is justified.

References p. 167.

Re 1. The disturbances which may influence atomization and mist formation, in general comprise all the disturbances originating in a difference in viscosity, surface tension, pH, or in temperature between standard solution and solution under test. The factors mentioned may play a part in the process of atomization; the rate of atomization (*i.e.* the amount of fluid, aspirated per minute by the atomizer) as well as the yield (*i.e.* the fraction of the aspirated solution which reaches the flame as a mist) may be influenced by them, so that the emission is no longer constant.

It appears for instance that the viscosity of the solutions used may decrease the atomization rate (observed in g/10 min) considerably, which leads to a weakening of the emission. The same influence was observed of differences in temperature, which probably must also partly be attributed to changes in viscosity.

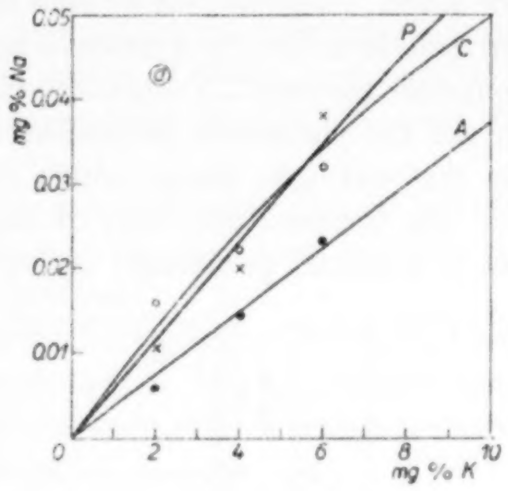
The influence of the surface tension of the fluid on the light emission was investigated by adding a quaternary ammonium base (desogen) as surface-active substance to the solution. No effect on the light emission was observed, although the surface tension varied from that of water (72 dyne/cm) to about 42 dyne/cm. Other investigators used substances like alcohol etc. to investigate the influence of the surface tension (BARNES *et al.*[2], HASLER[12], SMIT *et al.*[17]).

Here, however, a correlation, even though not linear, was indeed observed between an increase of the yield and a stronger emission. It is, however, difficult to find out whether substances like alcohol (of which a comparatively great amount must be added in order to change the surface tension considerably) exclusively influence the atomization process in that case. By burning alcohol in the flame the same effect is obtained as if more gas or less air are led to the flame, which causes, of course, a completely changed emission.

The body fluids saliva, blood serum and urine, which we analysed flame photometrically, were diluted 1:25, 1:50 and 1:25, respectively. These dilutions proved not to differ in viscosity and surface tension from the standard solutions used[19,23].

Re 2. The disturbances due to insufficient selectivity of the filters (the so-called filter-leakage) are caused by spectral light from elements present in the solution under test as admixtures. The following elements with an individual measurable emission are only present in body fluids such as saliva, blood serum and urine: sodium, potassium and calcium. As a check on these filter-leakage disturbances simple potassium and calcium chloride solutions were measured with the sodium filter so that in this way the given potassium and calcium concentrations could be evaluated as sodium values. Conversely, sodium and calcium chloride solutions could be measured in the same manner as potassium values with the potassium filter.

The disturbances of sodium by potassium and calcium, and those of potassium by sodium and calcium, determined as described above (for the concentrations of the elements to be considered) prove to be extremely small, for the acetylene flame as



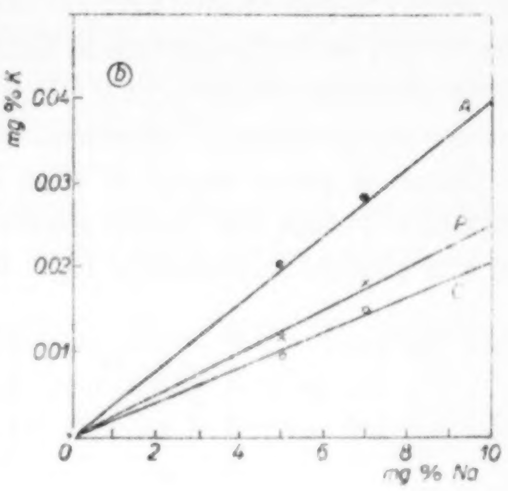


Fig. 4*a*. Disturbance of sodium by potassium due to filter-leakage. Determination of simple potassium chloride solutions with the sodium interference filter.
Abscissa: mg % K (as KCl)
Ordinate: Na-value found (in mg %)
• acetylene gas (A)
× propane gas (P)
o coal-gas (C)

Fig. 4*b*. Disturbance of potassium by sodium due to filter-leakage. Determination of simple sodium chloride solutions with the RG8 filter.
Abscissa: mg % Na (as NaCl)
Ordinate: K-value found (in mg %)
For explanation of the symbols, see Fig. 4*a*.

well as for the propane and the coal-gas flame; the error found is as a rule less than 1% (Fig. 4). When the content of the disturbing element is known this so-called additive disturbance can always be corrected.

Re 3. The first demands which should be made upon the flame for a good flame photometric analysis are: reproducibility of the light source and the constancy of the emission. The greatest source of errors in the flame photometric determination carried out without precautions is formed by the intrinsic flame disturbances.

These comprise all the disturbances caused by an influence on the process of atomic emission in the flame of the element under test by the ions and admixtures also present in the solution, and which disturbances cannot be abolished by filters.

Thus the presence of sodium may influence the intensity of the potassium emission, and conversely. In order to investigate these disturbances, we determined experimentally the influence of the various cations, anions, salts, acids and organic substances on the intensity of the sodium and potassium emission. As said before, acetylene, propane or coal-gas may be used in the flame. The acetylene flame has the highest temperature of these (about 2450° K), the temperatures of the propane and coal-gas flames are 300-400° lower. Therefore the sodium determination, carried out with the acetylene flame, proves to be 3 to 4 times as sensitive as when done with the propane or coal-gas flame; the calcium determination is even 7 to 9 times as sensitive. The sensitivity of the potassium determination in the coal-gas flame is about equal to that in the acetylene flame, which shows that the potassium atoms are easily excited; the temperature level of the coal-gas flame is apparently sufficiently high for a maximal potassium emission.

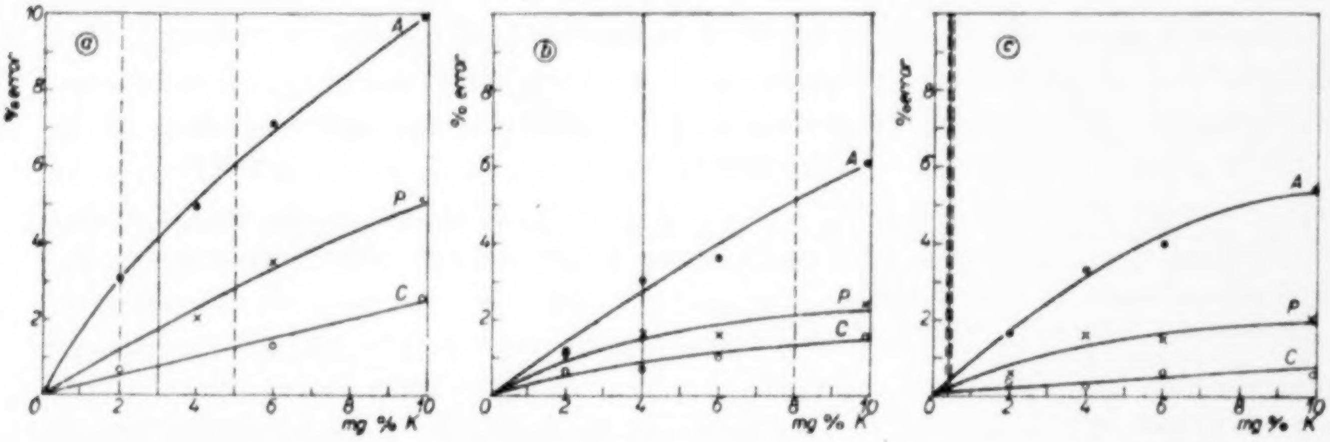


Fig. 5*a*. Determination of 2 mg % Na (saliva analysis). Effect of potassium.
Fig. 5*b*. Determination of 4 mg % Na (urine analysis). Effect of potassium.
Fig. 5*c*. Determination of 6 mg % Na (serum analysis). Effect of potassium.
Fig. 5. Sodium determination. Interference by potassium.
Abscissa: amount of potassium (added as KCl)
Ordinate: % error of the sodium value
- • acetylene gas (A)
- × propane gas (P)
- o coal-gas (C)

For further details, see also text.

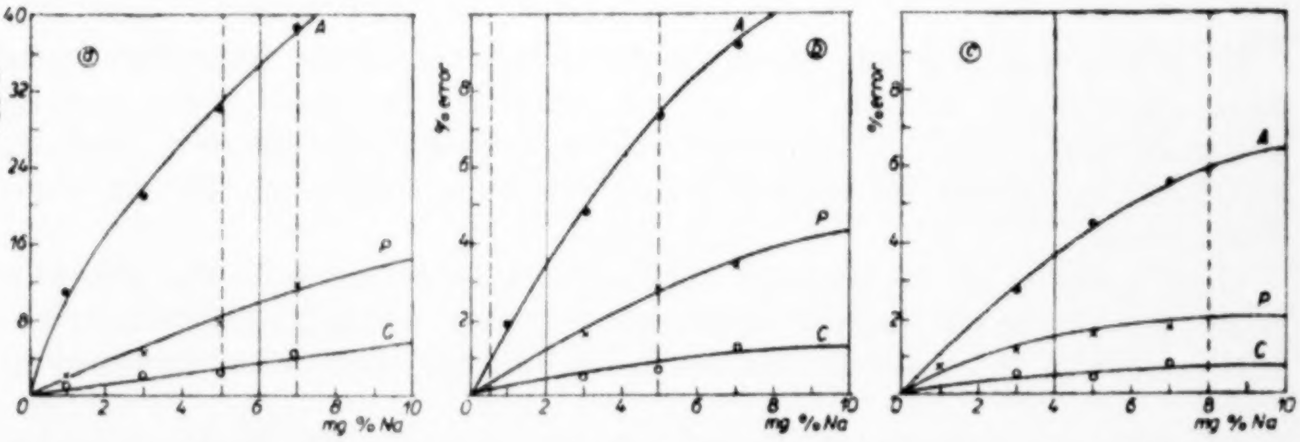


Fig. 6*a*. Determination of 0.4 mg % K (serum analysis). Effect of sodium.
Fig. 6*b*. Determination of 3 mg % K (saliva analysis). Effect of sodium.
Fig. 6*c*. Determination of 6 mg % K (urine analysis). Effect of sodium.
Fig. 6. Potassium determination. Interference by sodium.
Abscissa: amount of sodium (added as NaCl)
Ordinate: % error of the potassium value
For explanation of the symbols, see Fig. 5.

The following is a summary of the results of the sodium and potassium determinations, carried out with acetylene, propane and coal-gas, in solutions in which sodium, potassium, calcium and various admixtures (salts, organic substances) were simultaneously present (see also Figs. 5 and 6).

(a) There is a considerable mutual interference of sodium and potassium in the acetylene flame, becoming manifest in an increase of the sodium and potassium emission.
(b) The mutual interference mentioned under (a) occurs in the propane flame to a far lesser degree, in the coal-gas flame practically not at all.
(c) The interference effects become relatively smaller in higher concentrations of the disturbed cation.
(d) The interference effects become also relatively smaller in higher concentrations of the disturbing ion.
(e) The intensity of neither the sodium nor the potassium emission is disturbed by calcium either in the acetylene or in the coal-gas flame.
(f) A disturbance by acids (sulphuric acid) in the sodium and potassium determination manifests itself in a weakening of the emission.
(g) Disturbances of the sodium and potassium determination by the concentrations involved of anions, salts and organic substances did not occur in the coal-gas flame.

We preferred the coal-gas flame for the flame photometric analysis of sodium and potassium, in spite of the lesser sensitivity of the sodium determination, for the following reasons:

(1) Disturbance of potassium by sodium and conversely due to a mutual influencing of the process of excitation in the flame (as is observed in the acetylene flame) practically does not occur in the coal-gas flame.

(2) The sensitivity of the potassium determination does not decrease when acetylene is replaced by coal-gas.

(3) The disturbance of the sodium and potassium determinations by calcium (which is entirely due to filter-leakage) decreases when coal-gas is used. This may be explained by the fact that calcium is excited in the coal-gas flame only to a slight degree. Therefore, when coal-gas is used, this effect is completely negligible for the given calcium concentrations in the body fluids investigated.

(4) Further it is a pre-requisite that the apparatus used possess the greatest reliability, as it must be possible to entrust the carrying out of the flame photometric sodium and potassium determinations in body fluids to personnel with less experimental skill, as a routine procedure. This was another reason for preferring coal-gas to acetylene.

The composition of the coal-gas fom the municipal gas works is not liable to great variations: the average caloric value of this gas is about 4000 ± 75 kcal/m^3, so that a practically constant flame temperature will be obtained in spite of these slight variations. Application of the method of interpolation, however, makes us completely independent of possible variations in caloric value (see p. 157).

Sodium and potassium were used as semi-internal standard elements for a general check-up of disturbances (see p. 156). To this end a given amount of sodium or potassium was added to the diluted solution under analysis, following which it was flame photometrically investigated which percentage of this addition was recovered. Moreover we investigated the influence of various dilutions of the sample under analysis on the results of the determination, in which it appeared that very high dilutions (higher than 1:400) gave incorrect, as a rule too high, figures.

We chose the dilutions 1:25 and 1:50, for saliva and blood serum, respectively. The choice is facultative for urine; the dilution of 1:25 as well as 1:50 can be used here; we used mainly the first dilution. The sodium as well as the potassium determination can be carried out with this simple dilution[23].

When bearing in mind the possible slight mutual disturbances of sodium and potassium, we may use elementary standard solutions, exclusively containing sodium and potassium, for the flame photometric analysis of saliva, blood serum and urine by means of the coal-gas flame. The possible mutual filter-leakage disturbance of sodium and potassium is relatively small, and can be almost completely counteracted by adding the average quantity of the accompanying element to the standard solutions.

Table I mentions the average sodium, potassium and calcium contents in saliva, blood serum and urine, with at the same time the variations in concentration of these elements, pathological cases included.

TABLE I

SODIUM, POTASSIUM AND CALCIUM CONTENT (IN MG %) OF SALIVA, BLOOD SERUM AND URINE

Solution under investigation	Sodium		Potassium		Calcium	
	average	variation	average	variation	average	variation
saliva	50	10-120	75	60-100	4	2-8
blood serum	325	250-350	20	10-30	10	5-15
urine	200	0-500	150	0-400	15	0-30

Taking into account this composition, we may use the standard solutions, as given in Table II, for flame photometric analysis in diluted saliva (1:25), diluted serum (1:50), and diluted urine (1:25 or 1:50, respectively).

As said before, when we consider the extremely low concentrations of calcium,

TABLE II

STANDARD SOLUTIONS FOR THE EXAMINATION OF SALIVA, BLOOD SERUM AND URINE

saliva 1:25		blood serum 1:50		urine 1:25 or 1:50	
Na-scale (with in every solution 3 mg % K)	K-scale (with in every solution 2 mg % Na)	Na-scale (with in every solution 0.4 mg % K)	K-scale (with in every solution 6 mg % Na)	Na-scale (with in every solution 4 mg % K)	K-scale (with in every solution 4 mg % Na
0.5 mg % Na	2.0 mg % K	5.0 mg % Na	0.30 mg % K	1.0 mg % Na	1.0 mg % K
1.0 ,, ,,	2.5 ,, ,,	5.5 ,, ,,	0.35 ,, ,,	2.0 ,, ,,	2.0 ,, ,,
1.5 ,, ,,	3.0 ,, ,,	6.0 ,, ,,	0.40 ,, ,,	3.0 ,, ,,	3.0 ,, ,,
2.0 ,, ,,	3.5 ,, ,,	6.5 ,, ,,	0.45 ,, ,,	4.0 ,, ,,	4.0 ,, ,,
3.0 ,, ,,	4.0 ,, ,,	7.0 ,, ,,	0.50 ,, ,,	5.0 ,, ,,	5.0 ,, ,,
4.0 ,, ,,	5.0 ,, ,,			6.0 ,, ,,	6.0 ,, ,,
5.0 ,, ,,				7.0 ,, ,,	7.0 ,, ,,
				8.0 ,, ,,	8.0 ,, ,,

the disturbances by this element are negligible, so that no calcium has to be added to the standard solutions.

By taking into account the disturbances given in Fig. 4, 5 and 6, we can justify the use of these standard solutions. The sodium standard solutions are provided with the average quantity of potassium present in the solution under analysis, and conversely, sodium is added to the potassium solutions.

Tables III and IV show the maximal errors which may occur in the determination of sodium and potassium in diluted saliva, blood serum and urine, owing to a possible difference in composition between standard solution and solution under test (see also Figs. 5 and 6).

TABLE III

SODIUM DETERMINATION

mg % Na	in standard solution provided with	variation in K content of solution under investigation	greatest difference in K content between Na standard solution and solution under investigation	greatest error in %, caused by this difference in composition		
				acetylene	propane	coal-gas
2 mg % Na (saliva 1:25)	3 mg % K	2-5 mg %K	2 mg % K	2.0	1.1	0.5
4 mg % Na (urine 1:25 or 1:50)	4 mg % K	0-8 mg%K	4 mg % K	2.7	1.4	0.7
6 mg % Na (serum 1:50)	0.4 mg%K	0.3-0.5mg%K	0.1 mg%K	0.1	0.04	0.01

TABLE IV

POTASSIUM DETERMINATION

mg % K	in standard solution provided with	variation in Na content of solution under investigation	greatest difference in Na content between K standard solution and solution under investigation	greatest error in %, caused by this difference in composition		
				acetylene	propane	coal-gas
0.4 mg % K (serum 1:50)	6 mg % Na	5-7 mg%Na	1 mg%Na	3.2	1.3	0.5
3 mg % K (saliva 1:25)	2 mg% Na	0.5-5 mg% Na	3 mg % Na	4.0	1.6	0.4
6 mg % K (urine 1:25 or 1:50)	4 mg%Na	0-8 mg%Na	4 mg % Na	3.6	1.5	0.4

We learn from these tables that the possible error of the determination, carried out with coal-gas, is very small; however, if acetylene is used this error is too great to be neglected completely.

As mentioned before, the error caused by a mutual influencing of the sodium and potassium emission is relatively smaller for higher concentrations of the disturbing as well as of the disturbed element. When the coal-gas flame is used, application of the standard solutions according to Table II in the flame photometric analysis of saliva, blood serum and urine is practically always justified; therefore incidental preparation of standard solutions as a result of an important difference in sodium and/or potassium content between the solution under test and the standard solutions used will occur very rarely.

Thus for simple dilutions of the solution under analysis, the sodium and potassium determinations can be carried out with these standard solutions, by interpolation of the galvanometer deflection of the diluted test solution against those of two standard solutions.

The standard solutions are prepared from stock solutions. A stock solution of 100 mg % Na is obtained by dissolving 2.541 g NaCl (pro anal), powdered beforehand and dried for two hours at 105°, in a graduated 1000 ml flask in distilled water. From this the standard solutions of 1-10 mg % Na are prepared by stepwise dilutions. A potassium stock solution is prepared in the same way by dissolving 1.907 g KCl (pro anal) in 1000 ml distilled water.

To ensure the correct content of the standard solutions, we might prepare daily the required standard solutions from the stock solution, under the necessary precautions of cleansed glassware. Needless to say, such a procedure is extremely

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time-consuming. Therefore it is to be recommended to preserve the standard solutions for a longer period.

It is allowable to neglect in practice a possible transfer of sodium and potassium from the glass of the bottles to stock solutions of relatively high concentration, kept in them. However, when standard solutions are kept in these bottles for a longer period, an error may be made by neglecting this transfer completely. Therefore it is necessary to investigate the quality of the bottle material used for the preservation of the standard solutions.

We elaborated a method to investigate flame photometrically a possible transfer of sodium and potassium from the glass of bottles to fluids kept in them. For this investigation we had five different kinds of glass at our disposal, while poly-ethylene bottles were also examined. The results of this investigation are shown in Figs. 7 and 8; the correlation between the transfer and the time in days is indicated.

Jena, Pyrex and Leerdam glass prove to be suitable to preserve the standard solutions required for our investigation for at least six months — the period of time covered by our research. The transfer of sodium and potassium, observed for these three kinds of glass was negligibly small.

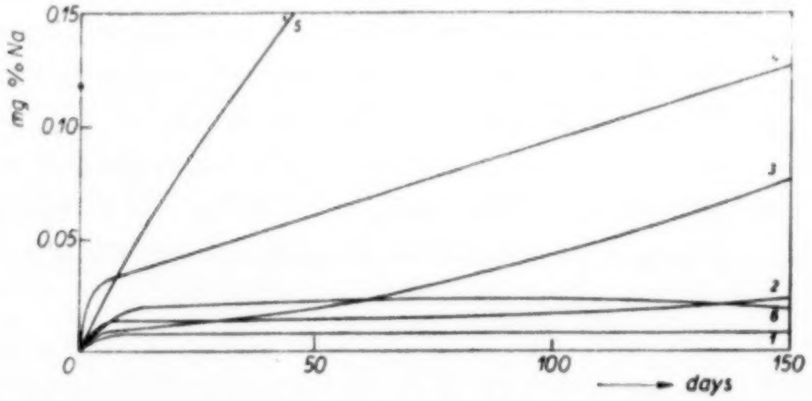

Fig. 7. Correlation between transfer of sodium to distilled water and time in days. (1) Jena, (2) Pyrex, (3) Leerdam, (4) medicine glass, (5) stoppered bottle, (6) poly-ethylene.

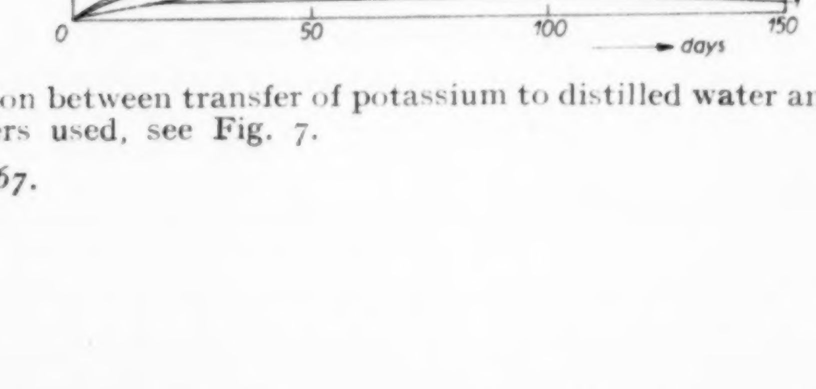

Fig. 8. Correlation between transfer of potassium to distilled water and time in days. For the numbers used, see Fig. 7.

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PRESCRIPTIONS FOR ANALYSIS

Standard solutions

Simple standard solutions may be prepared from stock solutions of 100 mg % Na and 100 mg % K (as the chloride, see p. 164) by stepwise dilutions. The standard solutions used by us contain sodium as well as potassium (see Table II). These solutions are prepared by adding together equal amounts of simple sodium and potassium standard solutions of double concentration. To prepare, for example, one litre of the potassium standard solutions of 2.0, 2.5, 3.0, 3.5, 4.0 and 5.0 mg % K, required for a saliva analysis, which solutions contain 2 mg % Na each, 500 ml of a 4 mg % Na solution is added to 500 ml K solutions of 4.0, 5.0, 6.0, 7.0, 8.0 and 10.0 mg % K, respectively.

These solutions are kept in bottles of Pyrex, Jena or Leerdam glass.

Apparatus

When starting an analysis, first the air and gas pressure are adjusted. The flame is ignited about thirty seconds after the opening of the gas cock. The flame, which has a length of about 10-12 cm, must be quite colourless, practically noiseless, and should not flicker. The disperser of the atomizer is fixed in such a manner that a maximal galvanometer deflection is obtained with any standard solution. The height of the burner before the condenser is determined in the same way.

Special care should be exercised that the pressures of coal-gas and air are constant. We mentioned before a method to obtain a constant coal-gas pressure by means of a combination of rubber balloons, automatic pressure regulator and needle valve; the regulation of the air flow is carried out with a 2-stage pressure reducing valve, regulation valve and needle valve.

Measuring method

The preparatory work on the saliva, serum and urine consists of simple dilution with distilled water, up to 1:25, 1:50 and 1:25, respectively.

The measurements are carried out by interpolation of the galvanometer values of the diluted solution under test against those of two standard solutions. About fifteen to twenty seconds after the beginning of a vaporization the equilibrium in the flame is established and the galvanometer value can be read off.

At the end of a serial analysis distilled water and alcohol are subsequently atomized, following which air is blown through for a short time, so that atomizer and burner are completely clean and dry.

A serial investigation was carried out with the above-described method of analysis in diluted saliva (see also ref. 20), diluted serum and diluted urine[23].

The results of these flame photometrical analyses showed a fair agreement with those of the usual clinical chemical methods for the determination of sodium and potassium.

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Summarizing, we may conclude that the very rapid and simple flame photometric method of analysis (which is moreover a highly sensitive micromethod) is much to be preferred to the troublesome, laborious and time-consuming chemical methods for the determination of sodium and potassium.

SUMMARY

A flame photometric method of analysis is described for the determination of sodium and potassium in saliva, blood serum and urine. The interference between various ions is discussed, employing flames of different temperatures (acetylene, propane and coal-gas).

RÉSUMÉ

L'auteur décrit une méthode d'analyse photométrique de flamme pour le dosage du sodium et du potassium dans la salive, le sérum sanguin et l'urine. L'influence de divers ions est examinée; on peut utiliser des flammes de différentes températures (acétylène, propane et gaz).

ZUSAMMENFASSUNG

Es wird eine flammenphotometrische Analysenmethode zur Bestimmung von Natrium und Kalium in Speichel, Blutserum und Urin beschrieben. Die Störungen der Ionen untereinander bei der Benützung von Flammen verschiedener Temperaturen (Acetylen-, Propan- und Stadtgas) wird besprochen.

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COULOMETRISCHE TITRATION*

von

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Durch seine Gesetze hat FARADAY die theoretische und experimentelle Grundlage für die elektroanalytischen quantitativen Bestimmungen geschaffen. Die Grundgesetze wurden später auf zwei verschiedenen Wegen für analytische Zwecke ausgewertet. Erstens hatte der elektrische Strom hauptsächlich für die quantitative Abscheidung von Metallen und Metalloxyden, die nachträglich gewogen wurden, analytische Anwendung gefunden (LUCKOW, CLAASSEN, TREADWELL, FISCHER, SAND), zweitens wurden auf Grund der Äquivalenz von chemischer Materie und Strommenge die nötigen Strommengen für eine bestimmte elektrochemische, bzw. chemische Umsetzung auf verschiedenen Wegen gemessen und daraus quantitative Schlüsse gezogen. Auf diese Weise konnten durch Messung des elektrischen Stroms die Mengen der in Lösung übergeführten Metalle oder Metalloxyde, oder aber die Mengen aus der Lösung abgeschiedener Metalle und Metalloxyde genau bestimmt werden. Eine besondere beachtenswerte Erweiterung erfuhr diese Arbeitsweise als man anfing an der Kathode oder an der Anode verschiedene bekannte primäre elektrochemische oder sekundäre chemische Reaktionen mit bekannter Strommenge auszuführen, wobei durch geeignete Indikatoren das Ende der Reaktion möglichst genau angezeigt wurde. Aus der Strommenge, die zur quantitativen Ausführung einer bestimmten elektrochemischen oder chemischen Reaktion benötigt wurde, konnte mit guter Genauigkeit die äquivalente Menge der chemischen Materie und dadurch auch die Menge der zu bestimmenden Verbindung berechnet werden.

Als die ersten Anfänge einer solchen quantitativen Ausnützung der Faradayschen Gesetze können folgende Verfahren erwähnt werden. QUINN und HULETT[45] haben schon 1914 eine Methode ausgearbeitet um mit in Reihe geschalteten Silber- und Cadmiumcoulombmetern das Äquivalentgewicht von Cadmium abzuschätzen. CAMPBELL UND THOMAS[6, 7], GROWER[23] und OGAREV[44] haben die coulometrische Methode dahin ausgenützt, dass sie die metallischen Überzüge elektrolytisch mit konstanter Stromstärke auflösten und dadurch die Möglichkeit schufen, auf Grund der bekannten Stromstärke und der gemessenen Zeitdauer die Dicke der aufgelösten Metallüberzüge zu berechnen. Dieselbe Methode hat auch FRANCIS[20] angewandt um die Dicke von metallischen Überzügen festzustellen.

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Die elektrolytische Auflösung der vorher abgeschiedenen Metalle zum Zwecke quantitativer analytischer Bestimmung, hat ZBINDEN[61] erstmalig ausgeführt und 10 bis 100 Mikrogramm Kupfer auf diese Weise bestimmt. Dieselbe Arbeitsweise wurde auch von ZAKHAREWSKII[60] angewandt, indem er zur Kupfer- oder Bleibestimmung zuerst aus der untersuchten Lösung das Kupfer bzw. das Bleidioxyd elektrolytisch niederschlug und dann durch eine genau gemessene Strommenge wieder auflöste, wodurch er auf die Menge der vorhandenen Metalle schliessen konnte. ELEMA[13] arbeitet auch nach dem Grundprinzip von ZBINDEN[61]. Jüngst wurde dasselbe Prinzip von LORD JR., O'NEIL UND ROGERS[32] für die elektrolytische Abscheidung und nachträgliche Auflösung von Submikrogrammen Silber angewandt. Es wurde ein Verfahren ausgearbeitet, das es ermöglicht auf diese Weise Mengen von Silber in den Grenzen von 10^{-8} g in 20 μl bis 25 ml mit einer Genauigkeit von 10^{-10} g zu bestimmen. Diese Methode erlaubt, nach der Angabe der Autoren, den Nachweis und die quantitative Schätzung von Silbermengen, die wenigstens zwanzigmal kleiner sind als diejenigen, die durch die beste Tüpfelreaktion von Feigl feststellbar sind.

Eine Arbeitstechnik, die Ähnlichkeit mit der coulometrischen Methode aufweist, ist die selektive Sauerstoffbestimmung in kleinen Gasmengen wie sie KORDESCH UND MARKO[26] durch Strommessung in einer Zelle, in welcher der zu bestimmende Sauerstoff eine Kohlenelektrode depolarisiert, ausgeführt haben.

HICKLING[24] hatte Bestimmungen mit begrenzten Kathoden- und Anodenpotentialen ausgeführt, wobei nur die gewünschte Reaktion eintreten konnte. Er lässt die Prozesse nur bis zum Erscheinen von residuellem Strom, der das Ende der Reaktion anzeigt ablaufen, wobei er die Strommenge mit einem Coulombmeter bestimmt. LINGANE[27, 28, 29, 30] hat die Methode von HICKLING für die quantitative Bestimmung von Kupfer, Wismuth und Blei durch Messung der Strommenge, die für die quantitative Metallabscheidung benötigt wurde, angewandt. Die durchgegangene Strommenge wurde mit einem Coulombmeter gemessen und die Arbeitselektroden wurden automatisch bei den entsprechenden Potentialen gehalten. Dabei wurde die Stromstärke ebenfalls konstant gehalten. LINGANE und JONES[31] haben auch einen elektromechanischen Integrator für coulometrische Analysen vorgeschlagen, der mit einer Genauigkeit von ± 1% arbeitet und bestimmt ist die chemischen Coulombmeter zu ersetzen.

Ausser diesen beiden quantitativen Auswertungen der Strommengen, die für die quantitative Auflösung von niedergeschlagenen Metallen oder Metalloxyden oder für die quantitative Abscheidung von Metallen benötigt wurden, fand diese Umkehrung der eigentlichen Coulombmeter besonders in den letzten Jahren eine breite Anwendung für die verschiedensten mikroanalytischen quantitativen Bestimmungen, für Reduktionen und Oxydationen an den Elektroden, bzw. für sekundäre chemische Umsetzungen, die an den Elektroden nachträglich ausgelöst werden.

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Ausgedehnte und zweckentsprechende Studien über die weitere und allgemeinere Anwendung der coulometrischen Methode haben SZEBELLEGY UND SOMOGYI[53] ausgeführt und durch ihre Arbeiten auch die unzweifelhafte breite und vielfache Anwendungsfähigkeit der coulometrischen Bestimmungen gezeigt. Sie haben mit elektrolytisch entwickelten Reagenzien quantitative Säure- und Basenbestimmungen, sowie Rhodanid-, Hydrazin- und Hydroxylaminbestimmungen ausgeführt, das Ende der gewünschten Reaktionen wie sonst üblich durch Indikatoren festgestellt und aus dem Gewichtszuwachs der Kathode im eingeschalteten Silbercoulombmeter auch die durchflossene Strommenge und dadurch auch die gesuchte Menge der zu bestimmenden Materie bestimmt. Obwohl die Methode wegen der Anwendung von Silbercoulombmetern etwas umständlich war, bot sie doch beachtenswerte Möglichkeiten für die analytische Auswertung der Faradayschen Gesetze.

EPSTEIN, SOBER UND SILVER[14] haben diese Methode für die Mikrobestimmung von Säuren in wässerigen Lösungen weiter ausgearbeitet. Um die umständliche Anwendung von Silbercoulombmetern zu vermeiden, haben sie mit konstanten, genau gemessenen Stromstärken gearbeitet, wodurch die Möglichkeit gegeben war, nur durch einfache Messung der Zeit mit Hilfe einer genauen Stoppuhr die durchgegangene Strommenge mit genügender Genauigkeit festzustellen und daraus die Menge der reagierenden Substanz zu berechnen. Durch diese Modifikation der anfänglichen Arbeitsweise wurde eine bedeutend breitere Möglichkeit für die weitere Anwendung dieser Methode gegeben.

Das Prinzip der eigentlichen coulometrischen Methode besteht darin, dass sich an der Kathode oder an der Anode in geeigneten Elektrolyten entweder primär elektrochemische Umwandlungen der zu bestimmenden Materie quantitativ in genau bekannter Weise mit 100 %-iger Stromausnützung abspielen, oder dass an den Elektroden quantitativ primär Stoffe in Freiheit gesetzt werden, die dann nachträglich, sekundär mit der zu bestimmenden Verbindung in genau bekannter Weise quantitativ reagieren. Kurz gesagt, es können verschiedene primäre oder sekundäre Oxydationen und Reduktionen an geeigneten Elektroden oder in ihrer unmittelbaren Nähe erzwungen werden, wobei man durch die Kenntnis der verbrauchten Strommenge auch auf die umgesetzte Substanzmenge mit grosser Genauigkeit schliessen kann. Diese Arbeitsweise hat im Grunde genommen eine gewisse Ähnlichkeit mit den sonst üblichen volumetrischen Titrationen. Während aber bei der volumetrischen Titration der untersuchten Lösungen genau abgemessene Volumina bestimmter Lösungen bekannter Konzentration zugegeben werden und das Ende der Titration durch geeignete Indikatoren festgestellt wird, um aus dem gemessenen zugegebenen Volumen auf die Menge der zu bestimmenden Substanz zu schliessen, gibt man nach dieser Methode den zu analysierenden Lösungen nicht vorher vorbereitete Lösungen bekannter Konzentration zu, auch hat man nicht ihre Volumina zu messen, sondern es werden die Coulombs dosiert, die nötig sind um eine bestimmte Elektrooxydation oder Reduktion an den Elek-

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troden zu bewerkstelligen, oder die nötige Menge der geeigneten Substanz in Freiheit zu setzen, die dann sekundär quantitativ reagieren soll. Anders gesagt, durch die Elektroden als Vermittler werden der zu untersuchenden Lösung die entsprechenden Materien allmählich zugegeben und ihre Menge aus der Menge von Coulombs, die gemessen wird, ermittelt. Ungeachtet der Art und Weise der allmählichen Zugabe und der Dosierung von Reagenzien, entweder durch eine Bürette oder sonstige Einrichtung, oder elektrochemisch durch Elektroden, kann diese Arbeitsweise eine Titration benannt werden, oder besser coulometrische Titration, weil eigentlich primär die Coulombs dosiert werden. Auf Grund ähnlicher Erwägungen haben auch unlängst Sease, Niemann und Swift[52] die coulometrische Titration als eine Bestimmungsmethode formuliert, durch die eine Substanz quantitativ durch elektrochemische Oxydation oder Reduktion, oder sekundär durch die elektrochemisch in Freiheit gesetzte Materie bestimmt wird, wobei die Messung der nötigen Coulombs entweder durch Abmessung der Materie in einem Coulombmeter, oder durch Messung der Durchflussdauer elektrischen Stroms bekannter, nach Möglichkeit konstanter Stärke geschieht.

Eine der Hauptbedingungen für die quantitative Ausführung coulometrischer Titrationen ist, dass sich die gewünschten elektrochemischen Oxydationen oder Reduktionen, bzw. die Entwicklung des benötigten Reagenzes mit 100 %-iger Stromausbeute abspielen. In Fällen, in welchen man auch Nebenreaktionen befürchten könnte, kann das Arbeiten mit begrenzten Elektrodenpotentialen zu gutem Erfolg führen, wie erstmals von Hickling[24] gezeigt und von Lingane weiter angewandt und ausgebaut wurde[27-30].

Die zweite Bedingung für die erfolgreiche Ausführung quantitativer coulometrischer Titrationen ist das genaue Einhalten konstanter Stromstärken während der Ausführung der Bestimmung, soweit man nicht mit Coulombmetern arbeitet [2, 35, 39]. Für Makrobestimmungen kann man die konstanten Ströme mit genügender Genauigkeit gewöhnlich mit Hilfe eines Potentiometers einer stärkeren Stromquelle entnehmen. In der letzten Zeit und vornehmlich für verschiedene Mikrobestimmungen, oder im Bestreben nach weitgehender Automatisierung, sind verschiedene automatische Einrichtungen zusammengestellt worden, die es ermöglichen mit wirklich grosser Genauigkeit eine bestimmte Stromstärke während der ganzen Dauer der Bestimmung einzuhalten[8, 19, 28, 29, 33, 36, 47, 49].

Der Endpunkt kann bei den coulometrischen Titrationen auf dieselbe Weise festgestellt werden, wie es auch sonst bei gewöhnlichen volumetrischen Titrationen geschieht. Es werden mit gutem Erfolg chemische Indikatoren angewandt[9, 18, 53, 55, 56], mit der Einschränkung, dass diejenigen nicht zu gebrauchen sind, die unter den gegebenen Arbeitsbedingungen an den Elektroden elektrolytisch reduziert oder oxydiert werden könnten. Diese Störungen können meistens vermieden werden durch Zugabe des Indikators erst in der Nähe des Endpunktes, wozu aber eine ungefähre Kenntnis der Lage des Endpunktes nötig ist. Die potentiometrische Endpunktbestimmung wird bei den coulometrischen Titrationen mit bestem Erfolg angewandt[9, 10, 14, 19, 21, 40, 41, 42, 54], genau so wie auch die amperometrische Methode immer mehr zur Anwendung kommt[3, 5, 15, 33, 37, 46, 52, 59]. Ähnliche Endpunktbestimmungen durch das Aufhören des Stroms an einer geeigneten Indikatorelektrode[22, 24, 27, 30], sowie die beiden vorhererwähnten Verfahren haben jetzt zu einer sehr weitgehenden Automatisierung der Arbeitsweise geführt, die in einigen Fällen höchstens einige Minuten des Arbeitenden für die Bestimmung in Anspruch nimmt[19].

Ein Nachteil der amperometrischen Endpunktbestimmungen besteht darin, dass dabei die coulometrischen Titrationen nicht mit stärkerem Elektrolysenstrom als 10 mA ausgeführt werden können, weil durch stärkere Ströme parasitäre Ströme an den Indikatorelektroden hervorgerufen und dadurch die genauen Bestimmungen des Äquivalenzpunktes unmöglich gemacht werden.

Die Möglichkeit einer sehr feinen Dosierung von Reagenzien, bzw. Coulombs, wie sie sonst durch eine Bürette, oder sonstige Einrichtung schwer oder gar unmöglich auszuführen wäre, ist durch die coulometrische Arbeitsweise gegeben. Für Mikrobestimmungen können heute coulometrisch Mengen von 10^{-12} Äquivalenten des Titrationsmittels zugegeben werden, wie neulich Cooke, Reilley und Furman[11] gezeigt haben, ja es erscheinen sogar auch Zugaben von 10^{-17} Äquivalenten als wohl möglich, wobei eine Verfeinerung der Zugabe durch immer feinere Strommessung zwar möglich ist, aber auch in der Ausnützung beschränkt wird durch nicht genügende Empfindlichkeit der Endpunktbestimmung, was auch sonst bei den Mikrobestimmungen eines der grössten Probleme ist[58]. Für eine solche übermässig kleine Dosierung wurde die amperometrische Methode zur Endpunktbestimmung durch Messung der Diffusionsströme, d.h. durch gleichzeitige Polarogrammaufnahme[11] bedeutend verfeinert.

Die Zeitmessung wird mit Handstoppuhren[14, 37, 40, 41, 55, 56] oder mit elektrischen Stoppuhren[9, 19], ausgeführt. Die erwähnten automatischen Einrichtungen ermöglichen heute die Einschaltung oder die Unterbrechung des Stroms mit einer Verzögerung von höchstens 0.001 sek., die auch bei mikroanalytischen Arbeiten gar nicht ins Gewicht fällt.

Galvanoelektrische Coulometrie

Um die Anwendung einer äusseren Stromquelle zu vermeiden, haben Oelsen, Graue und Haase[41, 42, 43] die Ströme eines kurzgeschlossenen galvanischen Elements für coulometrische Titrationen ausgenützt, und diese Arbeitsweise elektrolytisch-potentiometrische Bestimmungen benannt. Einer eingetauchten Platinnetzelektrode wird durch Kurzschliessen über ein empfindliches Amperemeter mit einer Zinkelektrode das geeignete Potential gegeben und durch die Eintauchtiefe der Lösungselektrode und ihre Änderung die nötige Stromstärke hervorgerufen und konstant gehalten[57]. Zur Vermeidung des Einflusses der Lösungselektrode auf die zu untersuchende Lösung, wurde sie mit einem durch Kollodiummembran abgeschlossenen Glasrohr umgeben, oder die Elektrode selbst wurde mit einer

Kollodiummembran überzogen. Auf diese Weise, durch Messung der Zeitdauer bei konstanter Stromstärke, konnten Säure- und Basenbestimmungen mit guter Genauigkeit ausgeführt werden, sowie Reduktionen von Mn(VII), Cr(VI) und V(V), durch Vermittlung von gleichzeitig galvanoelektrisch erzeugten Ferroionen[43]. Diese Arbeitsweise, die eine Vereinfachung der üblichen Methode der coulometrischen Titration mit äusserer Stromquelle bedeutet und bei einigen Mikrobestimmungen gute Resultate gibt, ist auf solche Fälle beschränkt, für die galvanoelektrisch erreichte Elektrodenpotentiale genügen. SCHLEICHER[50] hat unlängst gezeigt, dass man die innerelektrolytische Reduktion der Permangansäure in seinem Gerät zur inneren Elektrolyse[51], auch visuell verfolgen kann, nicht dagegen die der Chrom- und Vanadinsäure.

Ausserhalb der Zelle entwickelte Reagenzien

Bei verschiedenen coulometrischen Titrationen, wie z.B. bei Säure- und Basenbestimmungen, kommt es oft zu Störungen durch Oxydationen oder Reduktionen an den Elektroden, an denen sich nicht immer nur die eigentlichen, erwünschten Reaktionen abspielen, oder durch sekundäre unerwünschte chemische Einwirkung der entstandenen Substanzen, die die ganze Bestimmung unausführbar machen können. Sehr oft, und bei Säuren- und Basenbestimmungen an unlöslichen Elektroden immer, ist man genötigt den Anodenraum vom Kathodenraum abzutrennen um die gegenseitige Beeinflussung der Elektrolysenprodukte zu vermeiden, oder wenigstens einzuschränken. Um diese Unterteilung der Reaktionsgefässe, die manchmal unbequem ist, zu vermeiden und den störenden Einfluss der Reaktionsprodukte gänzlich auszuschalten, haben DEFORD, PITTS UND JOHNS eine Modifikation der coulometrischen Titration ausgearbeitet[17, 18, 19], die es ermöglicht, die für die titrimetrische Bestimmung nötigen Reagenzien nicht innerhalb der zu untersuchenden Lösung zu entwickeln, sondern ausserhalb derselben, wodurch die erwünschten Titrationen unabhängig und unbeeinflusst von den gekoppelten elektrochemischen Reaktionen an der anderen Elektrode ausgeführt werden können. Die Arbeitsweise besteht darin, dass der Elektrolyt, in dem das nötige Reagenz elektrochemisch erzeugt werden soll, durch ein Rohr mit zwei Schenkeln zufliesst. In den beiden Rohrschenkeln, in denen sich der zufliessende Elektrolyt fast gleichmässig verteilt, werden durch Elektrolyse an eingeschmolzenen Elektroden in dem vorbeifliessenden Elektrolyten die Reaktionsprodukte erzeugt, die ohne gegenseitige Vermischung durch die getrennten Rohrschenkel abfliessen. Je nach Bedarf kann man den Katholyten oder den Anolyten in die zu titrierende Lösung einfliessen lassen und durch die Zeitmessung bei konstanter Stromstärke und durch die übliche Endpunktbestimmung die gewünschten Titrationen mit mit guter Genauigkeit ausführen. Diese Arbeitsweise, die als eine Verfeinerung der Grundmethode in bestimmten Fällen grosse Vorteile bringen kann, ist auch schon automatisiert[19] und als solche für die Acidimetrie und Alkalimetrie angewandt worden.

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Acidimetrie und Alkalimetrie

Die erste Anwendung der coulometrischen Titration für die Säuren- und Basenbestimmung stammt von SZEBELLEGY UND SOMOGYI[53]. Schon sie haben erkannt, dass im Falle, wo mit unlöslichen Elektroden gearbeitet wird, der Kathodenraum in dem die Wasserstoffionen herauselektrolysiert, bzw. die Hydroxylionen in der sauren Lösung in der die Säure bestimmt werden soll, erzeugt wurden, von dem Anodenraum getrennt werden muss, da anderenfalls die an der Anode erzeugten Wasserstoffionen, bzw. die proportionelle Entfernung der Hydroxylionen die kathodische Reduktion rückgängig, d.h. die quantitative Bestimmung unmöglich machen würden. Durch Arbeiten mit getrennten Elektroden unter Zuhilfenahme von geeignetem Leitsalz konnten sie befriedigende Resultate erhalten. Dieselbe Methode mit getrennten Elektrolyten haben auch EPSTEIN, SOBER UND SILVER[14] für die Bestimmung von Mikromengen von Säuren in wässerigen Lösungen weiter entwickelt. Sie haben diese Methode hauptsächlich für die Bestimmung von sauren Gasen in der Luft gebraucht, die auch für automatische und kontinuelle Analysen dienen kann. An Stelle von Coulombmetern bedienten sie sich, bei konstanter Stromstärke, für die Bestimmung der Zeitdauer der ausgeführten Titrationen der Stoppuhr, und durch diese Vereinfachung mit der potentiometrischen Endpunktbestimmung nach PINKHOF, konnten sie 30 bis 150 μg Säure mit einem Fehler von etwa 10 % in ca. 20 Minuten bestimmen. Die coulometrische Bestimmung von Schwefeldioxyd, das durch Verbrennung des Schwefels aus dem Stahl gewonnen wurde, haben OELSEN UND GÖBBELS[40], ohne Anlehnung an Vorgänger, mit gutem Erfolg ausgeführt, wobei der Endpunkt ebenfalls potentiometrisch bestimmt wurde. Auf dieselbe Weise konnten OELSEN, GRAUE UND HAASE[41] auch die Kohlensäure, die durch Verbrennung des Kohlenstoffs in anorganischen und organischen Substanzen erhalten wurde, in Bariumchloridlösung coulometrisch titrieren und den Endpunkt potentiometrisch ermittlen. Die Säurebestimmungen, hauptsächlich die Bestimmungen von Schwefeldioxyd und Kohlendioxyd, hat OELSEN mit seinen Mitarbeitern[42, 43] auch ohne Anwendung von elektrischem Strom aus einer äusseren Stromquelle galvanoelektrisch, mit potentiometrischer Endpunktermittlung, ausgeführt. Wir[56] haben die Säurebestimmungen mit getrennten Elektrolyten mit sehr einfachen Mitteln schnell und genau ausgeführt und die Arbeitsbedingungen gegeben, unter welchen die störende Wanderung der Wasserstoffionen praktisch vollständig unterbunden werden kann.

Die übliche Abtrennung des Katholyten vom Anolyten durch eine halbdurchlässige Membran oder durch Agar-Heber haben DEFORD, JOHNS UND PITTS[19] bei der coulometrischen Säure- und Basentitration dadurch vermieden, dass sie automatisch ausserhalb der Zelle in dem Elektrolyten, der an den Elektroden getrennt vorbeifloss, die Hydroxyl- bzw. Wasserstoffionen elektrolytisch erzeugten und die auf diese Weise erhaltenen alkalischen oder sauren Lösungen getrennt

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abführten und gebrauchten. Die Trennung des Katholyten vom Anolyten bei der coulometrischen Säurebestimmung kann auch durch Anwendung geeigneter löslicher Anoden vermieden werden, wodurch die Säurebildung um die Anode gänzlich ausbleibt, wie es schon SZEBELLEGY UND SOMOGYI gezeigt haben[53]. Auch CARSON JR. UND ROY[9] gebrauchten eine lösliche Silberanode in einem gemeinsamen Elektrolysierraum, wobei sie der zu untersuchenden sauren Lösung Alkalibromide zugaben. Durch anodische Auflösung des Silbers wird die Sauerstoffentwicklung unterbunden. Die erzeugten Silberionen bilden mit den vorhandenen Bromionen nach Überschreitung des Löslichkeitsproduktes unlösliches Silberbromid, das sich abscheidet und, da es nicht hydrolisiert, den Endpunkt in keiner Weise beeinflusst. Dadurch konnten sie organische Säuren, in Anwesenheit von grossen Mengen Mineralsäuren coulometrisch in Isopropylalkohol und in Wasser, sowie Kohlensäure und saure Salze in etwa 10 Minuten mit guter Genauigkeit bestimmen. Die Versuche mit löslichen Anoden aus Cadmiumamalgam, Zinkamalgam, Kupfer, Quecksilber, Blei und Aluminium führten zu keinen befriedigenden Ergebnissen, wegen der Hydrolyse der gebildeten Salze, wobei auch Zusätze zur Komplexbildung keine Abhilfe brachten.

Halogenentwicklung

Ausser in der Acidimetrie und Alkalimetrie hat die coulometrische Titration auch für quantitative sekundäre Oxydationen durch anodisch primär intermediär entwickelte freie Halogene schon einige Anwendungen gefunden. Als erste Titrationen mit primär elektrolytisch entwickeltem Halogen können die coulometrischen Titrationen mit elektrolytisch erzeugten elementaren Brom, die SZEBELLEGY UND SOMOGYI ausgeführt haben, erwähnt werden[53]. Sie haben gezeigt, dass mit elektrolytisch erzeugtem Brom Rhodan, Hydrazin, Sulfit, Bisulfit und Hydroxylamin mit guter Genauigkeit bestimmt werden können. SEASE, NIEMANN UND SWIFT[52] haben die coulometrische Titration von Thiodiglykol mit elektrolytisch erzeugtem Brom in 50%-iger Essigsäure ausgeführt, wobei die Bestimmung des Endpunktes amperometrisch mittels eines Paars von Platinelektroden ausgeführt wurde. Mengen bis 1420 µg konnten im allgemeinen mit einer Genauigkeit innerhalb 0.5 % bestimmt werden. SCHAFFER JR., BRIGLIO JR. UND BROCKMANN JR.[49] haben die automatische coulometrische Titration von Phosgen in Luft mit Hilfe eines kontinuierlich arbeitenden Titrometers ausgeführt. Sie haben Luft mit konstanter Geschwindigkeit durch die Titrationsapparatur geleitet und Brom mit einer Schnelligkeit entwickelt, die genügte um die Reaktion von Brom mit dem Phosgendampf zu ermöglichen und in Gang zu halten. Auf diese Weise war der Entwicklungsstrom in jedem Augenblick ein kontinuierliches Mass für den Phosgendampf in der Luft. MYERS UND SWIFT[37] bestimmten Arsen durch Oxydation zu fünfwertigem Arsen durch elektrolytisch erzeugtes Brom, wobei der Endpunkt amperometrisch ermittelt wurde. Sie konnten auf diese Weise 30 bis 1000 µg Arsen mit einer Genauigkeit von 0.3 bis 1 % bestimmen. BROWN

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UND SWIFT[3] haben Antimon durch coulometrische Titration mit elektrolytisch erzeugtem Brom und amperometrische Ermittlung des Endpunktes bestimmt. Durch Vermittlung von intermediär entwickeltem Chlor haben WOOSTER, FARRINGTON UND SWIFT[59] die coulometrische Titration von Jod mit elektrolytisch erzeugtem Brom durchgeführt und dabei den Endpunkt amperometrisch bestimmt. Das Chlor haben sie als Mittelprodukt in 2*N* Salzsäure benutzt und dabei immer positive Fehler von 0.5 bis 1 % beobachtet, die sie durch mögliche Bildung von Jodmonochlorid zu erklären versuchten. Eine automatische coulometrische Titration von gasförmigen Verbindungen des Schwefels mit elektrolytisch erzeugtem Brom haben unlängst AUSTIN, TURNER UND PERSY[1] mit gutem Erfolg ausgeführt. Vor ganz kurzer Zeit haben BUCK UND SWIFT[4] Anilin in salzsaurer Lösung durch coulometrische Bromierung mit einem Überschuss von Brom quantitativ bestimmt. Da die Bromierung bis zum 2, 4, 6-Tribromanilin nicht mit genügender Geschwindigkeit vor sich geht, muss man mit Unterbrechungen und in Gegenwart von Kupfersulfat und überschüssigem Brom arbeiten, dass dann nachträglich, durch Poländerung, an derselben Elektrode mit coulometrisch erzeugten Cuproionen zurücktitriert wird. In einem Acetatpuffer mit pH = 4.5 ist die Reaktionsgeschwindigkeit zwischen Anilin und Brom genügend gross, so dass auch die direkte coulometrische Titration mit amperometrischer Endpunktbestimmung ausführbar ist. BUCK, FARRINGTON UND SWIFT[5] haben auch Tl(I) durch Oxydation zu Tl(III) coulometrisch bestimmt, mittels elektrolytisch in Lösungen von Alkalihalogeniden entwickeltem Brom oder Chlor, wobei der Endpunkt amperometrisch ermittelt wurde. Bei Proben, die 93 bis 1900 μg Tl(I) enthalten, liegt der mittlere Fehler unter 0.2 %.

Ausser dieser coulometrischen Bestimmung ist bis jetzt mit elektrolytisch unmittelbar erzeugtem Chlor nur noch eine Bestimmung bekannt, und zwar die coulometrische Bestimmung von dreiwertigem Arsen als Arsenit, mit amperometrischer Endpunktermittlung, nach FARRINGTON UND SWIFT[15]. Sie konnten 300 bis 800 μg mit einem Fehler von ± 0.2 % und 30 bis 100 μg mit einem durchschnittlichen Fehler unter 1 % bestimmen.

Elektrolytisch entwickeltes Jod wurde von RAMSEY, FARRINGTON UND SWIFT[46] und gleichzeitig von DEFORD, PITTS UND JOHNS[18] und TUTUNDŽIĆ UND MLADENOVIĆ[55] für die coulometrische Titration angewandt. RAMSEY, FARRINGTON UND SWIFT[46] haben dreiwertiges Arsen mit anodisch aus Kaliumjodid entwickeltem Jod durch amperometrische Endpunktbestimmung mit einem Fehler von ca. ± 0.2 % bestimmt, und DEFORD, PITTS UND JOHNS[18] haben ebenfalls Arsen mit ausserhalb der Zelle in Freiheit gesetztem Jod coulometrisch titriert. TUTUNDŽIĆ UND MLADENOVIĆ[55] haben die coulometrische Titration von Thiosulfat in Anwesenheit von Kaliumjodid, unter Anwendung von Stärke für die Endpunktbestimmung ausgeführt und dabei durch die Aufnahme von Stromspannungskurven und durch Messen von Potentialen der Arbeitselektroden auch den Beweis erbracht, dass die Oxydation von Thiosulfat unter den angeführten Bedingungen sekundär

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durch Oxydation durch das primär elektrolytisch entwickelte Jod bewirkt wird. Ohne jegliche Automatisierung der Arbeitsweise konnte gezeigt werden, dass diese Grundbestimmung der volumetrischen Jodometrie mit sehr einfachen Mitteln und mit guter Genauigkeit coulometrisch bequem ausgeführt werden kann.

Ceriion

Als ein anderes intermediäres, primäres Oxydationsmittel für coulometrische Titrationen wurde unlängst auch das vierwertige Ceriion für die Bestimmung von Ferroionen angewandt. FURMAN, COOKE UND REILLY[21] haben gezeigt, dass sich die elektrolytische Oxydation von dreiwertigem Ceriumion zu vierwertigem Ceriion quantitativ abspielt. Das elektrolytisch erzeugte Ceriion konnten sie auch für die quantitative Oxydation und Bestimmung von Ferroionen in Ferrosulfat coulometrisch ausnützen. Um den Einfluss des Luftsauerstoffs zu vermeiden, haben sie in einer Kohlendioxydatmosphäre gearbeitet und mit der potentiometrischen Endpunktbestimmung, bei konstanten bekannten Stromstärken, einen Fehler von nur 0.07 % erreicht. Dieser coulometrische Prozess kann, nach ihrem Vorschlag, auch für andere Titrationen mit vierwertigen Ceriumionen nützliche Anwendung finden. Dieselbe coulometrische Titration mit elektrolytisch erzeugten Ceriionen haben auch COOKE, REILLEY UND FURMAN[11] mit Ferroionenkonzentrationen von 0.01 μg in 1 ml und mit einer Empfindlichkeit von 0.001 μg Ferroionen pro 1 ml Lösung ausgeführt. Die Genauigkeit von 0.5 % auf 100 μg titrierter Ionen konnte durch elektrolytische Zugaben von etwa 10^{-12} Äquivalenten des Titrationsmittels erreicht werden, wobei auch eine neue empfindliche Methode für die Endpunktbestimmung ausgearbeitet wurde, die sich neben der amperometrischen Methode auch der gleichzeitigen Aufnahme der Diffusionsströme und der Auswertung der erhaltenen Polarogramme bedient. Leider lässt die Reproduzierbarkeit der Bestimmung von Mikrogrammen noch zu wünschen übrig.

Cuproionen

Ausser den angeführten Oxydationen wurden auch einige coulometrische Reduktionen mit an den Kathoden primär erzeugten Reduktionsmitteln ausgeführt. Als elektrolytisch erzeugtes Reduktionsmittel für die coulometrische Titration von Vanadium haben FOGELSON UND KALMYKOWA[16] einwertige Cuproionen angewandt. Dasselbe Reduktionsmittel für die coulometrische Titration von Chromat und Vanadat haben auch MEIER, MYERS UND SWIFT[33] in salzsaurer Lösung benutzt, die zur Stabilisierung des erzeugten Kuprochlorids diente. Der Vorteil dieser indirekten coulometrischen Titration besteht darin, dass die Stärke des Generatorstroms infolge der hohen Konzentration der Cuproionen zeitunabhängig ist. Die Stromstärke wurde während der Elektrolyse automatisch reguliert und der Endpunkt amperometrisch festgestellt. Für die Rücktitration

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von überschüssigem Brom bei der coulometrischen Anilinbestimmung haben Buck und Swift[4] ebenfalls die coulometrisch erzeugten Cuproionen gebraucht.

Ferroionen

Bedeutend mehr wurden bisher elektrolytisch erzeugte Ferroionen für die coulometrischen Titrationen gebraucht. Oelsen und Göbbels[40] führten zuerst die coulometrische Titration der Lösungen von Permanganat und Vanadat durch elektrolytische Reduktionen von Feriionen aus, wobei der Endpunkt potentiometrisch festgestellt wurde. Cooke und Furman[10] haben coulometrisch Lösungen von Ceriumsulfat und Kaliumbichromat mit elektrolytisch an der Platinkathode erzeugten Ferroionen titriert. Lösungen von Bichromat lassen sich nicht quantitativ an der Platinkathode reduzieren, aber die primäre Erzeugung von Ferroionen ermöglicht diese Bestimmung unter Zugabe kleiner Mengen von Phosphorsäure. Der Endpunkt wurde potentiometrisch, durch Anwendung eines Elektrodenpaars Platin-Wolfram, festgestellt. Ammoniummetavanadat in Lösungen von Ferrisulfat haben Furman, Reilley und Cooke[22] in der Weise coulometrisch titriert, dass sie die Grundlösung ohne die zu bestimmende Lösung bis zu einem erwählten Potential titrierten, die unbekannte Lösung zugaben und dann erst anfingen die eigentliche Bestimmung auszuführen. Durch Anlegung einer geeigneten EMK an die Indikatorelektrode und die entsprechende Normalelektrode und durch die Titration auf den Nullwert des Stromes, unter Zuhilfenahme eines sehr empfindlichen Galvanometers, kann man, nach ihren Angaben, eine fast unbegrenzte Empfindlichkeit der Bestimmung erreichen. Durch elektrolytisch erzeugte Ferroionen in Lösungen von Ferriammoniumsulfat haben Cooke, Reilley und Furman[12] coulometrisch Kaliumpermanganat und Mangansulfat titriert, wobei sie den Endpunkt elektrometrisch bestimmten. Reduktionen von Mn(VII) zu Mn(II), von Cr(VI) zu Cr(III) und von V(V) zu V(IV) durch Vermittlung von Ferroionen führten auch Oelsen, Göbbels, Haase und Graue in saurer Lösung mit[40] und ohne Anwendung einer äusseren Stromquelle[43] aus. Für die galvanische Erzeugung des nötigen Stromes bedienten sie sich des Elektrodenpaars Zn-Pt, das in die zu untersuchende Lösung eingetaucht war, wobei an der Platinelektrode die primäre Reduktion von Ferrionen stattfand und sekundär unter „katalytischer" Wirkung der erzeugten Ferroionen auch die weiteren schon angeführten Reduktionen. Dieselben Reduktionen von Ce(IV), V(V), $Cr_2O_7^{-2}$ und MnO_4^- mittels elektrochemisch gebildetem Ferroion als intermediären chemischen Reduktionsmittel, führte unlängst auch L. Meites[35] aus und bewies dadurch die Anwendbarkeit eines Millicoulombmeters nach Bogan, Meites, Peters und Sturtevant[2], das zwischen 0 und 70 μA mit einem Fehler von ca. 1 % arbeitet.

Unmittelbare Bestimmungen

Wesentlich anders, ohne Vermittlung von elektrolytisch gebildeten intermediären chemischen Reduktions- oder Oxydationsmitteln, führten MacNevin und

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BAKER[39] unmittelbare coulometrische Oxydationen von Fe(II) und As(III) in saurer Lösung an Platinanoden durch. Zur Bestimmung der durchgeflossenen Coulombs bei diesen Titrationen, von denen die Oxydation von As(III) in stark saurer Lösung schon früher vorgeschlagen war[38], gebrauchten sie Knallgascoulometer mit einem mittleren Fehler von 1 %. Dabei entwickelten sie auch ein neues Verfahren zur Ermittlung der durchgegangenen Coulombmenge bei dieser primären coulometrischen Analyse. Da die funktionelle Abhängigkeit des Logarithmus der Stromstärke von der Zeit für die Oxydation von Ferroionen linear ist, konnte aus dem Neigungswinkel und dem Ordinatenabschnitt, bzw. aus der Oberfläche unter der Kurve im Koordinatensystem, die Menge der durchgeflossenen Coulombs mit einem relativen Fehler von 2 % berechnet werden. Durch diese neue Methode der Stromintegration kann die vollständige Elektrolyse vermieden und die Berechnung der Resultate schon nach 10 bis 15 Minuten Elektrolysendauer ermöglicht werden.

Die weitere Ausarbeitung der coulometrischen Titrationsmethoden ist zur Zeit in vollem Flusse und es stehen bestimmt noch viele Anwendungen der schon ausgearbeiteten Verfahren und die Schaffung prinzipiell neuer Möglichkeiten bevor. Die ursprüngliche, ausserordentlich genaue, aber auch langwierige Arbeitsweise mit der coulometrischen Bestimmung der durchgeflossenen Strommenge ist durch die Anwendung konstanter Stromstärken und Messung der Zeitdauer schon vollständig überholt, was eine bedeutende Vereinfachung und auch Verfeinerung der Methode mit sich brachte. Die heutigen coulometrischen Titrationen weisen gegenüber den volumetrischen Titrationen ziemlich wichtige Vorteile auf, wovon einer darin besteht, dass sich keine Probleme der Bereitung, Titerfeststellung und der Aufbewahrung der Standardlösungen aufdrängen. Ausserdem ermöglicht die coulometrische Arbeitsweise sehr verschiedene Schnelligkeit der Titration, die sich in sehr weiten Grenzen der Reaktionsgeschwindigkeit, der gewünschten Dauer einer Titration, der gegebenen Genauigkeit der Stromstärke- und der Zeitmessung und der zu bestimmenden Substanzmenge und anderen Arbeitsbedingungen anpassen lässt, was durch Volumabmessung und Änderung der Konzentration des Titriermittels auf keinen Fall zu erreichen ist. Durch die Verfeinerung der Methoden für die Endpunktbestimmung und besonders durch die Möglichkeit auch bei den amperometrischen Endpunktbestimmungen mit stärkeren Strömen als 10 μA, was einer Schnelligkeit der Titration von etwa 10^{-4} mÄqu. pro Sekunde entspricht, zu arbeiten, wurde diese neue analytische Methode in den letzten Jahren immer mehr zu einer eigentlichen quantitativen Mikromethode ausgearbeitet, die bezüglich Schnelligkeit der Bestimmung, Genauigkeit und Empfindlichkeit wohl schwer zu übertreffen ist. Zu allen diesen Vorteilen gesellt sich auch die fast vollständige Automatisierung, die wir besonders amerikanischen Autoren zu verdanken haben, die es ermöglicht, besonders beim Arbeiten mit Submikromengen, jeden individuellen und subjektiven Einfluss des Arbeitenden auf die Endergebnisse auszuschalten. Obendrein

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ist auch die Möglichkeit gegeben mit ganz einfachen Mitteln, die auch in bescheidensten Laboratorien zu finden sind, immer noch genügend genaue und schnelle Titrationen auszuführen, und zwar Oxydationen und Reduktionen mit derselben bescheidenen Apparatur, so dass man sich die Freiheit nehmen darf, zu sagen, dass wir durch diese Arbeitsweise eine wirklich sehr ausbaufähige Möglichkeit bekommen haben, die einen starken Einfluss auf unsere bisherigen Arbeitsmethoden haben und unsere festgelegten Meinungen über die erreichbare Genauigkeit und Empfindlichkeit der analytischen Methoden vielleicht ändern wird. Wir sind uns dessen bewusst, dass dieser Methode auch Grenzen gesetzt sind und dass ihr verschiedene Mängel anhaften, aber wir dürfen dennoch die Meinung aussprechen, dass wohl die Zeit gekommen ist, sie allgemeiner einzuführen und noch schneller zu fördern, als es bis jetzt der Fall war, wo sie doch in den meisten Arbeitsgemeinschaften noch immer fast unbekannt ist und ungenügend ausgenützt wird.

Das Faradaysche Gesetz hat sich auch in dieser Richtung, in seiner zweiten analytischen Auswertung, als eine sichere Grundlage einer makro- und mikroanalytischen Schnellmethode mit bedeutenden Anwendungsmöglichkeiten erwiesen.

ZUSAMMENFASSUNG

Die coulometrischen Bestimmungen von den ersten Anfängen bis zu den neuesten Anwendungsformen wurden einer ausführlichen und kritischen Betrachtung unterzogen. Auf Grund der bisherigen Ergebnisse konnte die allgemeine Bedeutung und wahrscheinliche weitere Entwicklungsrichtung der heutigen coulometrischen Titrationen angedeutet werden.

SUMMARY

Coulometric determinations are reviewed in a critical and comprehensive manner from the first processes up to the modern forms of application. On the base of the hitherto existing achievements both the general importance and the further trend of development of the modern coulometric titrations could be indicated.

RÉSUMÉ

Les dosages coulométriques sont examinés d'une façon critique et détaillée, des premiers procédés jusqu' à leurs formes d'utilisation actuelles. S'appuyant sur les résultats existants, on indique l'importance générale et le développement futur du dosage coulométrique.

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COULOMETRISCHE TITEREINSTELLUNG UND BEREITUNG VOLUMETRISCHER STANDARDLÖSUNGEN

EIN VORSCHLAG

von

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Die coulometrische Titration, eine Umkehrung der eigentlichen Coulombmetrie, fand besonders in den letzten Jahren eine breite Anwendung und zwar immer mehr für verschiedene mikroanalytische quantitative Bestimmungen — Reduktionen und Oxydationen an den Elektroden, bzw. sekundäre chemische Umsetzungen, die an den Elektroden nachträglich ausgelöst werden. Unter der Bedingung, dass sich diese Prozesse quantitativ nach bekannten stöchiometrischen Verhältnissen abspielen, können durch sehr genaue Messungen der benötigten Strommengen, die heutzutage leicht und zuverlässig ausführbar sind, die reagierenden Substanzmengen mit ausserordentlich grosser Genauigkeit festgestellt werden. Auf diese Weise können der zu untersuchenden Lösung die gewünschten Materien durch die Elektroden als Vermittler allmählich zugegeben oder die chemischen oder elektrochemischen Reaktionen hervorgerufen, und ihre Menge aus der Menge der durchgegangenen Coulombs ermittelt werden. Während bei den volumetrischen Titrationen den untersuchten Lösungen genau abgemessene Volumina bestimmter Lösungen bekannter Konzentration zugegeben werden, um aus dem gemessenen zugegebenen Volumen auf die Menge der zu bestimmenden Substanz zu schliessen, gibt man nach dieser Methode den zu analysierenden Lösungen nicht vorher vorbereitete Lösungen bekannter Konzentration zu, auch hat man nicht ihre Volumina zu messen, sondern es werden mit grosser Feinheit die Coulombs dosiert, die nötig sind um eine bestimmte Elektrooxydation oder Reduktion an den Elektroden zu bewerkstelligen, oder die nötige Menge der geeigneten Substanz in Freiheit zu setzen, die dann sekundär quantitativ reagieren soll. Dabei ist die Möglichkeit einer sehr feinen Dosierung von Reagenzien, bzw. Coulombs, wie sie sonst durch eine Bürette, oder sonstige Einrichtung schwer oder gar unmöglich auszuführen wäre, gerade durch diese coulometrische Arbeitsweise gegeben. Für Mikrobestimmungen können heute coulometrisch Mengen von 10^{-12} Äquivalenten des Titrationsmittels zugegeben werden, ja es erscheinen sogar auch Zugaben von 10^{-17} Äquivalenten als wohl möglich[1], wobei eine Verfeinerung der Zugabe durch immer feinere Strommessung zwar möglich, aber

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auch in der Ausführung durch nicht genügende Empfindlichkeit der Endpunktbestimmung nach den heute üblichen Methoden beschränkt ist.

Die heutigen coulometrischen Titrationen weisen gegenüber den volumetrischen Titrationen Vorteile auf, wovon ein wesentlicher darin besteht, dass sich keine Probleme der Bereitung, Titereinstellung und Aufbewahrung der Standardlösungen als nötig erweisen. Ausserdem können coulometrische Titrationen, Titereinstellungen und Bereitungen von Grundlösungen mit sehr einfachen Mitteln schnell und mit grosser Genauigkeit ausgeführt werden. Zu allen diesen Vorteilen gesellt sich auch die fast vollständige Automatisierung, die es ermöglicht, für besondere Zwecke, jeden subjektiven Einfluss des Arbeitenden auf die Endergebnisse auszuschalten.

Alle diese Vorteile, die die coulometrische Arbeitsweise bietet, und die bisherigen Erfahrungen auf diesem Gebiet[2,3] in Betracht ziehend, scheint uns der Vorschlag berechtigt, durch eine internationale Kommission Vorlagen auszuarbeiten, auf Grund deren in Zukunft die Titereinstellung und Bereitung volumetrischer Titrierlösungen nicht mehr mit Lösungen, die durch Abwägen von chemischer Materie bereitet wurden, sondern entweder nur, oder vorläufig auch, coulometrisch erfolgen soll. Mit anderen Worten ginge der Vorschlag dahin, an Stelle irgendeiner chemischen Substanz das Coulomb als Ursubstanz in die gesammte Volumetrie einzuführen.

Unserer Meinung nach ist dafür heute die coulometrische Arbeitsweise die zuverlässigste und ermöglicht zweifellos Einheitlichkeit, Genauigkeit und Sicherkeit, wodurch eine weitgehende Verfeinerung und Vereinfachung der Grundlösungbereitung und Eichung erreicht werden könnte.

Genau so wie das Coulomb auf Grund der Faradayschen Gesetze als die Grundlage für die Festlegung und Bestimmung von int. Ampere schon seit Jahrzehnten dient, sollte es auch durch internationale Vereinbarung in die Volumetrie und in die analytische Chemie überhaupt, als das genaueste Grundmass für die genaueste Abmessung von chemischer Materie eingeführt werden.

ZUSAMMENFASSUNG

Es wird der Vorschlag gemacht, das Coulomb als Ursubstanz an Stelle irgendwelcher chemischen Substanz in die gesammte Volumetrie einzuführen.

SUMMARY

It is proposed to introduce the coulomb as a standard, instead of one or other chemical reference substance, for all volumetric operations.

RÉSUMÉ

L'auteur propose d'introduire le coulomb comme référence, au lieu de n'importe qu'elle substance chimique, pour toutes les opérations titrimétriques.

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COULOMETRISCHE BESTIMMUNG VON THIOSULFAT

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Die volumetrische Bestimmung von Thiosulfat und die schnelle und genaue Titerfeststellung von Thiosulfatlösungen, die grundlegende Bedeutung für die gesammte Jodometrie haben, stossen auf einige Schwierigkeiten, hauptsächlich was die Bereitung und Erhaltung von Jodgrundlösung anbetrifft. Um diese Schwierigkeiten zu vermeiden und die genaue und schnelle Titereinstellung von Standardthiosulfatlösungen mit einfachen Mitteln und ohne vorherige umständliche und nicht immer genaue Bereitung von Jodlösungen zu ermöglichen, haben wir die coulometrische Arbeitsweise[1] auf diese Bestimmung angewandt. Es hat sich gezeigt, dass unter gewissen Bedingungen die coulometrische Thiosulfatbestimmung schnell und zuverlässig mit einfachen Mitteln sehr gute Resultate gibt, was die Einführung dieser Titration in die gesammte Jodometrie rechtfertigt.

Elektrolytisch entwickeltes Jod haben unlängst auch RAMSEY, FARRINGTON UND SWIFT[2] und DEFORD, PITTS UND JOHNS[3] fast gleichzeitig mit uns für die coulometrische Titration angewandt. RAMSEY, FARRINGTON UND SWIFT haben dreiwertiges Arsen mit anodisch aus Kaliumjodid entwickeltem Jod durch amperometrische Endpunktbestimmung mit einem Fehler von *ca.* ± 0.2% bestimmt, und DEFORD, PITTS UND JOHNS haben ebenfalls Arsen mit ausserhalb der Zelle in Freiheit gesetztem Jod coulometrisch titriert.

Im Falle, dass das durch Elektrolyse einer Kaliumjodidlösung primär quantitativ entstandene Jod auch genügend schnell ohne Nebenreaktionen mit der vorher zugegebenen Menge von Thiosulfat unter Bildung von Tetrathionat als Endprodukt und unter Rückbildung von Jodionen reagiert, könnte diese Bestimmungsweise Vorteile für die gesammte Jodometrie mit sich bringen. Beim Arbeiten mit konstanter Stromstärke könnte dann durch Messung der Zeit mit genügender Genauigkeit die Menge der Coulombs, bzw. des zu bestimmenden Thiosulfats, auf Grund des bekannten stöchiometrischen Verhältnisses, bestimmt werden. Das Ende der Reaktion liesse sich dann durch Zugabe von Stärkelösung oder potentiometrisch scharf erkennen.

Bei der Elektrolyse einer wässerigen Lösung von Thiosulfat an unangreifbaren

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Elektroden mit und ohne Kaliumjodid, könnte die Oxydation von Thiosulfat auf verschiedenen Wegen von statten gehen. Es kann ohne Mitwirkung von Jodionen die unmittelbare Oxydation von Thiosulfat an der Anode, oder die sekundäre Oxydation durch ausgeschiedenen Sauerstoff aus den primär oxydierten Hydroxylionen eintreten. Dem Mechanismus dieser Oxydationen sind bereits mehrere Untersuchungen gewidmet. THATSCHER[4] z.B. formulierte die Reaktionen an der Anode wie folgt

$$\begin{aligned} O^{-2} - 2\,(-) &\longrightarrow 1/2\ O_2 \\ 2\ S_2O_3^{-2} + 1/2\ O_2 &\longrightarrow S_4O_6^{-2} + O^{-2} \end{aligned}$$

wobei Sauerstoff- bzw. Hydroxylionen regeneriert werden und das pH auf diese Weise konstant auf seinem anfänglichen Wert bleibt. Die Formulierung Thatschers könnte in dem Falle angenommen werden, wenn die Geschwindigkeit der eigentlichen Thiosulfatoxydation durch Sauerstoff gleich der Geschwindigkeit der elektrochemischen Oxydation von Sauerstoff-, bzw. Hydroxylionen an glatter Platinanode wäre, was aber nicht der Fall ist, weswegen eine grössere Menge von Sauerstoff gebildet als verbraucht wird, was zur gleichzeitigen teilweisen Sauerstoffentwicklung führt. Auf diese Weise wird die Lösung immer saurer und ausserdem kommt es dadurch auch zu unerwünschten Nebenreaktion. An platinierter Platinanode haben bis zu einem gewissen Potential beide Reaktionen gleiche Geschwindigkeiten, und da das Potential dabei unverändert bleibt, kann daraus gefolgert werden, dass sich tatsächlich die angenommenen Reaktionen abspielen. GLASSTONE UND HICKLING[5] stimmen der Annahme THATSCHERS der indirekten Oxydation von Thiosulfat zu, sind aber der Meinung, dass es dabei unter gewissen Bedingungen zur Bildung von Wasserstoffperoxyd kommt, das die Oxydation von Thiosulfat grösstenteils in Tetrathionat und wenig Sulfat bewirkt. Beim Überschreiten jener Peroxydmenge, die gerade für die normale Oxydation von Thiosulfat ausreicht, sowie unter den Bedingungen unter denen die Zerlegung vom Wasserstoffperoxyd beschleunigt wird, kann es zur Sauerstoffentwicklung kommen, die vollkommen überwiegen kann.

Während der Elektrolyse von Natriumthiosulfatlösungen in Gegenwart von Kaliumjodid bleibt das Anodenpotential konstant und unter diesen Bedingungen bildet sich kein Sauerstoff, wie schon Thatscher beobachtet hat. Auf Grund dieser Beobachtung hat er sich den Mechanismus in Anwesenheit von Kaliumjodid wie folgt vorgestellt

$$\begin{aligned} &1)\ O^{-2} + 2\,(+) \ \ldots\ldots\ldots\ldots\ 1/2\ O_2 \\ &2)\ 1/2\ O_2 + 2\ J^- \ \ldots\ldots\ldots\ldots\ J_2 + O^{-2} \\ &3)\ J_2 + 2\ S_2O_3^{-2} \ \ldots\ldots\ldots\ldots\ S_4O_6^{-2} + 2\ J^- \end{aligned}$$

Während man der Folgerung Thatschers, sowie der von Glasstone und Hickling, dass es nicht zu der unmittelbaren Oxydation des Thiosulfats an der Anode kommt, zustimmen kann, muss die oben von Thatscher angeführte Reihenfolge der Reaktionen abgelehnt werden.

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Beim Vergleich der Abscheidungspotentiale einschliesslich der Überspannungen von Sauerstoff und Jod, in den in Betracht kommenden Lösungen, kann man als primäre Produkte der Elektrolyse an der Anode Jodatome und Moleküle erwarten und nicht Sauerstoff, obwohl dabei auch die Möglichkeit der Bildung von Wasserstoffperoxyd in Betracht gezogen werden muss. Um zu der experimentellen Entscheidung über den Mechanismus der Thiosulfatoxydation in Anwesenheit von Kaliumjodid und die Eignung der elektrolytischen Entwicklung von Jod für die quantitative coulometrische Titration von Thiosulfat zu kommen, haben wir durch direkte Messung an glatter Platinanode, wie es sonst üblich ist, Stromdichte-Potentialkurven aufgenommen und zwar in Lösungen von Kaliumjodid verschiedener Konzentration, in Lösungen von Natriumthiosulfat verschiedener Konzentration und in Lösungen mit verschiedenen Mengenverhältnissen von Kaliumjodid zu Natriumthiosulfat bei verschiedenen Konzentrationen. Es zeigte sich dabei, wie dies aus der Tabelle I, die einen Auszug aus den erhaltenen Resultaten darstellt, hervorgeht, dass die Potentiale der Platinanode, auf die Stromdichte 0 Amp/cm^2 extrapoliert, in reinen Lösungen von Kaliumjodid je nach der Konzentration von + 0.535 bis + 0.60 V variieren und in Lösungen von reinem Natriumthiosulfat, je nach der Konzentration, zwischen + 1.22 und + 1.28 V liegen, was von grundlegend verschiedenen Anodenprozessen zeugt. In Lösungen, die gleichzeitig Kaliumjodid und Natriumthiosulfat in verschiedenen Mengenverhältnissen enthalten, ändert sich mit der Konzentration das Potential der Arbeitsanode von + 0.53 bis + 0.565 V, was zweifellos den Beweis erbringt, dass sich auch in Anwesenheit von Natriumthiosulfat, unter den angeführten Bedingungen, an der Anode derselbe primäre Prozess abspielt, wie in reinen Kaliumjodidlösungen, und zwar, allem Anschein nach, die Oxydation von Jodionen zu elementarem Jod, das nachträglich in atomarem oder molekularem Zustand auf das anwesende Thiosulfat unter Bildung von Tetrathionat und Rückbildung von Jodionen einwirkt.

TABELLE I

0.1 N KJ	+ 0.535 V
0.01 N KJ	+ 0.60
0.1 N $Na_2S_2O_3$	+ 1.22
0.01 N $Na_2S_2O_3$	+ 1.28
0.1 N KJ 0.1 N $Na_2S_2O_3$	+ 0.53
0.1 N KJ 0.02 N $Na_2S_2O_3$	+ 0.53
0.01 N KJ 0.01 N $Na_2S_2O_3$	+ 0.565

Bei der elektrolytischen Oxydation von Thiosulfat in neutralen Lösungen an

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platinierten Platinanoden beobachtete THATSCHER[4] Potentialwerte von + 0.47 bis + 0.67 V und stellte dabei fest, dass bei negativeren Potentialen bis + 0.644 V ausschliesslich Tetrathionat, wogegen bei positiveren Potentialen in steigendem Ausmass auch das Sulfat gebildet wird.

Nach den bisherigen Untersuchungen der Reaktion von Thiosulfat mit Jod in Kaliumjodidlösung scheint festzustehen, dass sich dabei als eines der intermediären Produkte das Jon $S_2O_3J^-$ bildet [6, 7, 8, 9]. Es zeigt sich dabei[9], dass in den Grenzen des experimentellen Fehlers, bei höheren Konzentrationen von Jodionen das gesammte gebildete Jon $S_2O_3J^-$ in das Jon $S_4O_6^{-2}$ übergeht, wogegen bei niedrigeren Jodionenkonzentrationen auch eine andere Reaktion in Erscheinung tritt, als welche die Bildung von SO_4^{-2} Jonen angenommen wird, wobei das stöchiometrische Verhältnis von Jod zu Thiosulfat teilweise verschoben wird. Nach KOLTHOFF[7] wird bei Titrationen von 10^{-3} M Jodlösungen, wenn das pH grösser als 5 ist, das Tetrathionat nicht nach dem sonst üblichen stöchiometrischen Verhältnis gebildet. Als Erklärung dafür nimmt er die Bildung von Sulfation durch Reaktion von Thiosulfat mit HOJ, die durch Jodhydrolyse in schwach sauren Lösungen entsteht, an.

Über die Wirkungsweise von anodisch erzeugten Jodatomen und Jodmolekülen mit dem Thiosulfat, das bis zum Äquivalenzpunkt stets im Überschuss vorhanden ist, können wir keine begründeten Aussagen machen. Ob es dabei zur Bildung von Tetrathionat über dieselben oder anderen Zwischenprodukte kommt, bleibe dahingestellt, jedenfalls, ungeachtet der Folge der Reaktionen, verlaufen die Grundreaktionen in den Grenzen der experimentellen Fehler quantitativ, wie wir experimentell nachgewiesen haben, sodass sich darauf die coulometrische Bestimmungsmethode von Thiosulfat mit elektrolytisch entwickeltem Jod begründen und ausarbeiten liess.

Für die experimentelle Ausführung dieser Bestimmung mussten auch einige Vorbedingungen erfüllt werden, die durch das elektrochemische und chemische Verhalten von Lösungen von Kaliumjodid, Thiosulfat und gebildetem Tetrathionat gegeben sind. Wegen der Unbeständigkeit der Thiosulfate, auch in ganz schwach sauren Lösungen, durfte die Lösung von Jodkalium, in der das Thiosulfat zu bestimmen war, während der Bestimmung nicht sauer werden. Andererseits durfte die Grundlösung auch nicht alkalisch sein oder es während der Ausführung der Bestimmung werden, wegen der Unbeständigkeit des Tetrathionats, welches, wie bekannt, in alkalischer Lösung in Sulfit und Bisulfit unter teilweiser Rückbildung von Thiosulfat zerfällt. Da beim Arbeiten in fast neutralen Lösungen keine Schwierigkeiten entstehen und keine störenden Nebenreaktionen stattfinden, und da die Lösungen von Kaliumjodid mit Thiosulfat neutral sind, bestanden keine Bedenken über die Möglichkeit der Ausführung dieser coulometrischen Titration.

Bei der Elektrolyse wässriger Lösungen von Kaliumjodid und Thiosulfat in einem Reaktionsraum an unangreifbaren Elektroden, z. B. an glatten Platin-

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elektroden, können sich an den Elektroden mehrere Reaktionen abspielen. An der Anode kommt es, wie schon gezeigt wurde, zur Abscheidung von elementarem Jod und nachträglicher Reaktion desselben mit dem vorhandenen Thiosulfat. Die Hauptbedingung wäre dabei, das Anodenpotential so einzuhalten und durch genügende Konzentration von Kaliumjodid dafür Sorge zu tragen, dass keine Abscheidung von gasförmigem Sauerstoff eintreten kann. An der Kathode werden die Wasserstoffionen bis zu elementarem Wasserstoff reduziert und ausgeschieden, unter Zurücklassung einer äquivalenten Menge von Hydroxylionen in der Nähe der Kathode. Durch diese Erhöhung der Hydroxylionenkonzentration kann in einem Elektrolysierraum das Abscheidungspotential an der Anode so weit verschoben werden, dass es auch zu gleichzeitiger Sauerstoffabscheidung kommt. Ausserdem können dann in der alkalischen Lösung aus dem schon gebildeten Tetrathionat Natriumsulfit und Natriumthiosulfat rückgebildet werden, und zu alldem kann der entstandene Wasserstoff selbst das gebildete Tetrathionat wieder in Thiosulfat zurück reduzieren, oder es könnte unter Umständen unmittelbar an der Kathode zu dieser Reduktion kommen. Auf diese Weise kann wenigstens teilweise ein Kreisprozess entstehen, was jedenfalls dazu führen würde, dass die Oxydation von Thiosulfat an der Anode unter diesen Bedingungen nicht quantitativ zu Ende geführt werden könnte.

Auf Grund solcher Überlegungen sind wir zu dem Ergebnis gekommen, dass diese coulometrische Titration in einem gemeinsamen Elektrolyten nicht quantitativ ausführbar ist, und dass sie sich dagegen wohl ausführen liesse unter Abtrennung des Anolyten vom Katholyten, was auch experimentell bestätigt wurde.

Experimentell wurde die coulometrische Titration von Thiosulfat an spiralenförmigen glatten Platinelektroden (0.7 mm × 45 cm) mit getrenntem Katholyten und Anolyten ausgeführt. Das Katholyten-, bzw. Anolytengefäss bildeten zwei kleine Glasbecher von ungefähr je 100 ml Fassungsvermögen, die durch eine Agar-Agar-Brücke mit Kaliumchlorid verbunden waren. An Stelle einer Agar-Brücke kann zuweilen auch ein elektrolytischer Schlüssel mit einem Hahn, gefüllt mit konzentrierter Kaliumchloridlösung, dessen Enden mit Filterpapierstopfen oder mit halbdurchlässigen Membranen verschlossen sind, dienen. Die Bestimmungen sind sehr bequem bei kleinerem Innenwiderstand auch in zwei röhrenförmigen Gefässen ausführbar, die durch eine halbdurchlässige Membran aus Glasfritte getrennt sind. Beim Arbeiten mit halbdurchlässigen Membranen wird durch die Saugwirkung des Rührers während der Bestimmung ein kleiner Teil des Katholyten in den Anodenraum eingesaugt, was ohne jeglichen Nachteil auf die Resultate bleibt, soweit man nur den Katholyten nicht ansäuert, sondern neutral erhält. Diese ganze Zusammenstellung wird in den Stromkreis eingeschaltet, der von einer Stromquelle mit potentiometrischer Stromabnahme mit automatischer Stromregelung oder einem groben und einem feinen Gleitwiderstand, einem Stromunterbrecher und einem genauen, geeichten, empfindlichen

Milliampermeter mit grosser Skala und mit der Möglichkeit der Ablesung von Zehntel bis Hundertstel Milliamper, gebildet wird. Der Kathodenraum wird während der Titration mit einem gewöhnlichen Laboratoriumsrührer mässig gerührt. Als Katholyt dient eine schwach saure, etwa 1-2%-ige Kaliumchloridlösung, die erst nach mehreren Bestimmungen und nach wiederholtem Ansäuern gewechselt zu werden braucht, und die nicht gerührt werden muss. Der Anolyt wird von der zu untersuchenden Thiosulfatlösung (etwa 2-10 ml 0.1 N $Na_2S_2O_3$ in etwa 80 ml Wasser) gebildet, der auf 100 ml 0.2 bis 1 g Kaliumjodid zugegeben wird. Durch eine Reihe unabhängiger Messungen konnte festgestellt werden, dass die Konzentration des Kaliumjodids keinen Einfluss auf die Genauigkeit der Resultate ausübt, solange sie nicht unter 10^{-3} N wird. Die Qualität des gebrauchten Jodkaliums hat ebenfalls keinen Einfluss auf die Endergebnisse, soweit es keine reduzierbaren Beimengungen oder Oxydationsmittel enthält. Die Proben mit verschiedenen Präparaten von Jodkalium, bis zum technischen, bewährten sich gleich gut. Da die Geschwindigkeit der primären, sowie der sekundären Reaktion an der Anode gross ist, spielt auch die Geschwindigkeit der Jodentwicklung keine wesentliche Rolle und man kann je nach dem Thiosulfatgehalt und der Konzentration mit verschiedenen Stromstärken arbeiten, um eine befriedigende Dauer der Bestimmung zu erreichen.

Zur Endpunktbestimmung wird dem Anolyten schon von Anfang an ein wenig lösliche Stärke zugegeben. Während der ersten Hälfte der Bestimmung ist auch in der unmittelbaren Nähe der Anodenspirale keine Spur einer Blaufärbung zu bemerken, aber mit dem Fortschreiten der Bestimmung und dem teilweisen Verbrauch des vorhandenen Thiosulfats zeigen sich an der Anode tiefblaue Schlieren, die zuerst in unmittelbarer Nähe der Anode verschwinden, um später trotz mässigen Rührens immer weiter in die Lösung vorzudringen. Dies ist auch ein Zeichen dafür, dass man sich dem Endpunkt nähert, der sich klar und deutlich durch plötzliche schwache und gleichmässige Blaufärbung des ganzen Anolyten anzeigt. Unter Zuhilfenahme einer weissen Unterlage ist es leicht die erste gleichmässige Färbung des Elektrolyten zu erkennen und das Ende der Titration genau zu bestimmen.

Ohne automatische Stromregelung und unter Anwendung einer gewöhnlichen Handstoppuhr beträgt der mittlere Fehler ± 0.02 bis ± 0.20%, je nach der Menge des zu bestimmenden Thiosulfats. Tabelle II gibt einen kleinen Auszug aus den erhaltenen Resultaten unter verschiedenen Bedingungen.

In demselben Anolyten, in dem eine Probe von Thiosulfat coulometrisch bestimmt wurde, können noch weitere Proben von Thiosulfat, ohne Zugabe von weiteren Mengen von Kaliumjodid und löslicher Stärke, coulometrisch titriert werden. Im Falle, dass eine von den Proben übertitriert wird, kann der Anolyt mit einem winzigen Tropfen ganz verdünnter Thiosulfatlösung entfärbt werden und weitere Titrationen können eine nach der anderen, ohne Zeit- und Materialverlust, ausgeführt werden. Auf diese Weise wird der ohnehin kleine Verbrauch

TABELLE II

Katholyt	Anolyt	Coulombs	Fehler %
	2 ml 0.1*N* $Na_2S_2O_3$	19.53	+ 0.01
	80 ml H_2O	19.51	— 0.10
	0.2 — 1 g KJ	90.35	+ 0.18
1 — 2 g KCl	5 ml 0.1*N* $Na_2S_2O_3$	48.97	+ 0.18
80 ml H_2O	75 ml H_2O	48.90	+ 0.04
H_2SO_4 (HCl)	0.2 — 1 g KJ		
	10 ml 0.1*N* $Na_2S_2O_3$	90.16	— 0.03
	70 ml H_2O	90.30	+ 0.12
	0.2 — 1 g KJ	97.52	— 0.14
		97.73	+ 0.07

von Jodkalium noch bedeutend verringert, was besonders bei Serienbestimmungen eine Rolle spielen kann und zugleich einen nicht zu unterschätzenden Zeitgewinn bedeutet.

Dieselbe coulometrische Thiosulfatbestimmung kann ohne irgendwelche prinzipielle Änderung auch als Mikro- und Submikrobestimmung ausgeführt werden, was nur von dem zu erreichenden Zweck, von der Empfindlichkeit der automatischen Stromregelung und von der Zeitmessung abhängt.

Die coulometrische Thiosulfatbestimmung und Titereinstellung mit elektrolytisch aus Kaliumjodid entwickeltem Jod hat sich unter verschiedenen Arbeitsbedingungen gut bewährt und stellt eine bequeme und zuverlässige Möglichkeit zur Ausführung dieser Grundtitration, ohne vorherige Bereitung und Eichung von Jodlösungen dar, was zweifellos einen Vorzug bedeutet. Diese coulometrische Titration, wie wir sie ausgeführt haben, kann unserer Meinung nach, die praktische Anwendung der Jodometrie sehr fördern, einesteils weil durch ihre Anwendung der Gebrauch von Jodlösungen mit genau festgestelltem Titer überhaupt vollständig vermieden werden kann, und zweitens weil diese Arbeitsmethode es ermöglicht elektrolytisch sehr genau den Titer von Thiosulfatlösungen festzustellen, die dann weiter mannigfaltig in der Jodometrie verwendet werden können. Auf Grund der weit genaueren Eichmöglichkeit der Grundlösungen durch Abmessen von Coulombs, an Stelle von chemischer Materie, kann auch der Vorschlag gemacht werden, die Eichung von Thiosulfatlösungen künftig auch nur coulometrisch auszuführen und das Coulomb als Ursubstanz in die Titrimetrie einzuführen[10].

Auf dieselbe Weise ist auch die Möglichkeit gegeben, nach Bedarf, in Lösungen von Kaliumjodid Jodlösungen mit genau bekanntem Jodgehalt elektrolytisch, ohne Anwendung von umständlich gereinigtem elementaren Jod zu bereiten.

Die coulometrische Thiosulfatbestimmung wird jetzt in unserem Institut weiter bearbeitet und es werden verschiedene Anwendungen dieser Methode experimentell geprüft.

Literatur S. 191.

ZUSAMMENFASSUNG

Es wurde die Methode der coulometrischen Bestimmung von Thiosulfat durch elektrolytisch aus Kaliumjodid entwickeltem Jod ausgearbeitet. Je nach der Feinheit der Stromregelung und der Zeitmessung ist sie für Makro-, Mikro- und Submikrobestimmungen anwendbar. Ausserdem ermöglicht sie die vorherige Bereitung und Anwendung von Jodlösungen gänzlich zu vermeiden.

Auf Grund dieser Möglichkeiten wird der Vorschlag gemacht den Titer von Thiosulfatlösungen von nun an nur elektrolytisch durch Messung der benötigten Coulombs zu bestimmen, und das Coulomb als Ursubstanz in die Volumetrie einzuführen.

SUMMARY

A method is developed for the coulometric determination of thiosulphate with iodine electrically generated from potassium iodide. Depending on the fineness of the regulation of the current and of the measurement of the time, the method is applicable to determinations in the macro, micro and submicro range. Moreover, with this method, the previous preparation and utilisation of iodine solutions can be avoided entirely.

Owing to these possibilities it is proposed to standardize thiosulphate solutions henceforward electrolytically by the measurement of the coulombs needed. Furthermore it is proposed to introduce the coulomb into the volumetric analysis as a standard.

RÉSUMÉ

Une méthode a été développée pour le dosage coulométrique du thiosulfate de sodium au moyen de l'iode libéré par l'iodure de potassium, électrolytiquement. Suivant la précision du réglage du courant et de la mesure du temps, la méthode est applicable aux dosages à l'échelle macro, micro et submicro. En outre, il est possible d'éviter la préparation préalable et l'utilisation de solutions d'iode.

Partant de ces possibilités, les auteurs proposent de déterminer dorénavant le titre des solutions de thiosulfate de sodium, uniquement par voie électrolytique, par la mesure des coulombs nécessaires, et d'introduire le coulomb comme base de la volumétrie.

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SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Ordinary Meeting of the Society

An Ordinary Meeting of the Society, organised by the Physical Methods Group, was held at 6.30 p.m. on Friday, January 30th, 1953, in the Mason Theatre, The University, Edmund Street, Birmingham. The Chair was taken by the President Dr. J. R. NICHOLLS, C.B.E., F.R.I.C. The subject of the meeting was *Chromatography* and the following papers were presented and discussed:

Chromatography Past and Present, by TREVOR I. WILLIAMS, B.A., B.Sc., D. Phil.

Far from being a modern discovery, chromatography, with the exception of ion exchange chromatography, has been applied in many different fields of chemistry for at least a century. That it has been widely, indeed universally, used only during the last fifteen years may be attributed to the fact that only comparatively recently have many problems arisen for which chromatography has unique advantages over older and well established methods.

Inorganic paper chromatography was intensively studied by RUNGE about 1850 and many of his original chromatograms are still extant. In the nineteenth century he was followed by SCHOENBEIN and GOPPELSROEDER, and in the early twentieth century by GRUSS. Modern interest in it, however, stems from the work of MARTIN AND SYNGE. The originators of adsorption chromatography were DAY, ALBRECHT AND ENGLER, and TSWETT, though as early as 1850 the soil chemists THOMPSON and WAY were perfectly familiar with the separations that occur on columns of adsorbent. Modern interest stems from the application of the method in the carotenoid field initiated by LEDERER and KUHN. Ion exchange chromatography was developed during the last war when it proved of immense value for isolating the tiny quantities of fission products resulting from the various atomic projects; it also revolutionized the chemistry of the rare earths.

There are now few fields of chemical analysis in which chromatography in one of its three principal forms has not proved equal to or superior to conventional methods. In the inorganic field an alternative to conventional group analyses has been found in paper chromatography. In organic analysis it has proved especially valuable in examining complex natural products, such as food and drink, in which unidentifiable constituents often interfere with normal tests. In the biochemical and medical field chromatography has been used in the analysis of such diverse substances as vitamins, hormones, antibiotics, drugs and alkaloids; especially important is the application to urine analysis. The ready availability of radioactive isotopes has proved an important development, most particularly in paper chromatography. Chromatography in the gas phase has received some attention and proved very valuable in the inert gas field, but undoubtedly much progress can be made here; indeed, this is perhaps the most promising field for future progress.

Inorganic Chromatography on Cellulose. Part XIV. The Quantitative Separation of Rhodium, Palladium, Iridium and Platinum, by D. B. REES-EVANS and R. A. WELLS, B.Sc., A.R.I.C.

The separation of the platinum metals has hitherto involved a complicated procedure of precipitation, solution and reprecipitation. A new method was presented which utilises the principles of partition chromatography, in obtaining a quantitative separation of rhodium, iridium, platinum and palladium. The process, which employs cellulose as the adsorbent and organic solvents as eluting agents, is relatively speedy and is capable of reducing the concentration of one metal in another from 50 to <0.001 per cent. in one operation. When dealing with a mixture of all four metals a solution of the sodium chloro-salts is freshly prepared in chlorine water and the platinum, palladium and iridium are then separated from rhodium in a cellulose column by extraction with a ketonic solvent. Suitable precautions are necessary throughout the separations to ensure that the metals remain in the same valency state and same salt form. The mixture of platinum, palladium and iridium is treated with sulphuric and perchloric acids and transferred to a second column, where, under suitable conditions platinum and palladium are extracted in acetone solution, from the iridium. The platinum, palladium mixture, after conversion to nitrate solution, is finally transferred to a third column and palladium is extracted from platinum with an ether, nitric acid mixture.

Radioactive tracer technique, together with spectrographic analysis and separations by paper strip chromatography, have been used to determine the efficiency of the separations. The process has been tested with the ratio of one metal to another varying from 1 : 1 to 100 : 1. Experiments have normally been carried out with 0.2 g quantities of the mixed metals but larger scale separations with 2 g of the metals have been successfully completed.

Chromatography of the Carbohydrates and their Derivatives, by J. K. N. JONES Ph.D., D.Sc.

Within recent years, considerable advances have been made in the separation and quantitative analysis of carbohydrates and of their derivatives. These advances have been made possible, in the main, by the discovery of paper partition chromatography; adsorption chromatography has also been found to be a useful analytical tool.

The sugars may be separated on sheets of paper by use of solvent mixtures which are acidic, neutral or basic in reaction. In general, acidic solvents are used to separate acidic and neutral sugars, basic solvents, in which most acidic sugars are immobilised, are used to separate basic and neutral sugars, and neutral solvents are used to separate neutral sugars. Phenol-water mixture is a solvent in which the relative rates of movement of sugars are greatly altered. The sugars are detected (1) by virtue of their reducing power, (2) by conversion to coloured derivatives with aromatic amines, (3) by oxidation with periodate solution, (4) by formation of coloured compounds, or (5) by use of radioactive isotopes. They may be estimated on the paper and determined after extraction from the paper. Larger amounts of sugars may be separated on columns of cellulose or starch, or by fractionation of their borate complexes on ion exchange resin or by adsorption on columns of charcoal. This latter method and the technique of adsorption of the sugars or of their derivatives on siliceous earths have provided the means to separate oligosaccharides containing up to seven sugar residues. The acidic sugars (uronic acids) may be adsorbed on basic resins and eluted with acid, while the basic sugars may be adsorbed on acidic resins and eluted with bases; thus it is possible to separate the sugars into basic neutral and acidic fractions and then to fractionate them further as described above. The sugars of higher molecular weight may be fractionated, under favourable conditions, by electrophoresis on paper using the apparatus of DENT. These techniques and their limitations were discussed.

The meeting was preceded by an afternoon visit to the Dunlop Research Centre, Dunlop Rubber Company Ltd., Fort Dunlop, Birmingham 24.

Annual General Meeting of the Scottish Section

The Eighteenth Annual General Meeting of the Scottish Section of the Society of Public Analysts and Other Analytical Chemists was held at 12.30 p.m. on Wednesday, January 28th, 1953, in the Rhul Restaurant, 123 Sauchiehall Street, Glasgow.

The following were elected Officers of the Section for the forthcoming year:

Chairman — Mr. R. S. WATSON, F.R.I.C.
Vice-Chairman — Dr. F. J. ELLIOTT, F.R.I.C.
Hon. Secretary & Treasurer — Mr. J. A. EGGLESTON, B.Sc., A.R.I.C., Boot's Pure Drug Co. Ltd., Motherwell Street, Airdrie, Lanarkshire.

Annual General Meeting of the North of England Section

The Twenty-eighth Annual General Meeting of the North of England Section of the Society of Public Analysts and Other Analytical Chemists was held at 2 p.m. on Saturday, January 31st, 1953, at the Engineers' Club, Albert Square, Manchester. The Chairman, Mr. A. A. D. COMRIE, B.Sc., F.R.I.C., presided over an attendance of thirty-seven.

The following were elected Officers of the Section for the ensuing year:

Chairman — Mr. T. W. LOVETT, F.R.I.C.
Vice-Chairman — Mr. J. R. WALMSLEY, A.M.C.T., F.R.I.C., Ph.C.
Hon. Secretary & Treasurer —Mr. ARNOLD LEES, F.R.I.C., 87, Marshside Road, Southport, Lancs.

The Annual General Meeting was followed by an Ordinary Meeting at which Mr. A. A. D. COMRIE delivered his Chairman's Address, the subject being *Beer Foam*.

Annual General Meeting of the Microchemistry Group

The Ninth Annual General Meeting of the Microchemistry Group of the Society of Public Analysts and Other Analytical Chemists was held at 7 p.m. on Thursday, January 29th, 1953, at the Sir John Cass College, London, E.C. 3.

The following were elected Officers of the Group for the ensuing year:

Chairman — Dr. A. M. WARD, F.R.I.C.
Vice-Chairman — Dr. G. F. HODSMAN, A. Inst. P.
Hon. Secretary — Mr. D. F. PHILLIPS, A.R.I.C., 101, South Promenade, St. Annes-on-Sea, Lytham St. Annes, Lancs.
Hon. Treasurer — Mr. G. INGRAM, A.R.I.C.

After the business meeting, the retiring Chairman, Dr. Cecil L. WILSON, F.R.I.C., addressed the meeting on *Microchemistry: An Appraisal*. This was followed by a discussion.

During the afternoon preceeding the meeting a party of members visited the new factory and laboratories of Messrs. L. Oertling Ltd. at St. Mary Cray, Orpington, Kent.

Physical Methods Group:

Symposium on "Developments in Microscopical Methods"

The above symposium will be held on *Friday, March 20th*, 1953, at *King's College, Strand, London, W.C.* 2. This is a joint meeting arranged by the Royal Microscopical Society (Industrial Section) in collaboration with the Institute of Physics, the Physical Society and the Physical Methods Group of the Society of Public Analysts and Other Analytical Chemists.

The arrangements are as follows:

2.20 p.m. Opening of the Symposium by Professor J. T. RANDALL, F.R.S.
2.30 p.m. *The Use of the Polarising Microscope in Organic Chemical Research*, by Dr. A. E. J. VICKERS.
Chairman, Brigadier J. SMITH, President R.M.S.
4 p.m. Tea Interval.
4.30—6 p.m. Session of Short Papers.
Testing Microscope Objectives with a Sheared Wave Front Interferometer, by M. G. L. CURTIES.
Solid Quartz Reflecting Objective of 0.90 N.A., by Dr. M. H. F. WILKINS.
A Use of the Polarising Microscope in X-ray Analysis, by E. G. STEWARD.
Polarisation of Fluorescence in Crystals, by Dr. R. BARER.
Influence of Illuminating Aperture on Optical Images, by Dr. H. H. HOPKINS.
Chairman, Dr. MARY DEMPSEY.
6.15 p.m. *Cinephotomicrography*, by Dr. A. H. HUGHES.
Chairman, Dr. M. H. F. WILKINS.

The President of the R.M.S. will close the Symposium.

There will be an exhibition which will be open from 2 p.m. throughout the afternoon and evening in the Laboratories of King's College.

REVUE DES LIVRES

Substances naturelles de synthèse, collection publiée sous la direction de L. VELLUZ, volume IV par J. MATHIEU, A. PETIT, P. POIRIER, L. VELLUZ — Masson et Cie, éditeurs, Paris, 1952, 165 pages, 2 hors-textes de microphotographies. Broché 1800 fr. cartonné toile 2200 fr.

Nous avons déjà rendu compte dans cette revue des trois premiers volumes de cette belle collection qui traite de la synthèse accompagnée de notes fort utiles, de corps biologiques importants. Ce quatrième volume traite de l'acide D-panthothénique, de la riboflavine, du ribose, de la testostérone, du DL-α-tocophérol. Comme méthodes de travail, les auteurs nous présentent cette fois, la cyclisation pyridique et la chromatographie classique par adsorption avec la manière de traiter l'alumine et de l'étalonner. En tableaux, on trouve indiqués, avec la bibliographie, les mélanges adsorbants à choisir pour séparer deux corps déterminés ainsi que l'indication des substances éluantes. L'ouvrage s'achève par des tableaux de correspondance entre les unités anglaises et françaises et les rapports entre les mailles des tamis.

L'ouvrage est très bien présenté; l'impression est claire, les figures nettes; l'index se montre commode. Si j'envisage le point de vue de l'analyste pur maintenant, je formulerai deux voeux timides pour l'avenir: 1° l'indication du grossissement des cristaux au microscope pour qu'on puisse les reproduire à coup sûr, 2° l'énumération succinte des caractères analytiques des corps préparés et notamment les réactions colorées.

CLÉMENT DUVAL (Paris)

Tablet making (La fabrication des comprimés) par ARTHUR LITTLE ET K. A.MITCHELL The Northern publishing Co. Ltd. Liverpool, England. 2 ème tirage 1951, 121 pages, 41 figures, relié 15 shillings franco.

Livre fort bien présenté, illustré de photographies très nettes représentant les machines, les parties de machines, les différentes formes de moules et de comprimés. La fabrication est décrite avec luxe de détails par des praticiens et englobe l'installation, le malaxage, la granulation, la fabrication à la main, la coloration, etc. C'est un livre que nous croyons indispensable pour tous ceux, pharmaciens et industriels, qui veulent fabriquer plusieurs milliers de comprimés à l'heure et les présenter au public d'une manière impeccable.

CLÉMENT DUVAL (Paris)

Les Théories Electroniques de la Chimie Organique, par B. PULLMAN et Mme A. PULLMAN, Masson & Cie. Paris, 1952, 665 pages, 170 fig. 107 tableaux, 5800 Fr. fr.

Il n'est pas rare d'entendre d'excellents praticiens émettre des avis de ce genre: ,,Ces théories électroniques sont très intéressantes, mais donnent un peu l'impression de vues de l'esprit assez éloignées des problèmes concrets qui se posent au chimiste. Elles ne sauraient par exemple jouer le rôle attendu de toute théorie: prévoir des faits nouveaux''.

C'est donc tout particulièrement à ces sceptiques que nous aimerions signaler ce remarquable ouvrage. Le mérite des auteurs est grand, qui, grâce à une excellente ordonnance d'un sujet fort complexe, ont su démontrer les extraordinaires possibilités de la Théorie Electronique.

Après un bref rappel des fondements de la mécanique ondulatoire (25 p.), base de la théorie, le lecteur est amené au calcul de l'atome (30 p.). Dans le cas général, la résolution rigoureuse dépassant les moyens mathématiques actuellement connus, une place est faite aux diverses approximations conduisant à des résultats numériques. Ces notions sont ensuite appliquées à l'étude des liaisons chimiques (62 p.) (divers types de valences, liaisons multiples et localisées, mésomérie) et des molécules conjuguées (100 p.). L'énergie de résonance (114 p.) fait l'objet d'un chapitre particulièrement captivant grâce à ses incidences sur les problèmes d'équilibres chimiques, de potentiel rédox et acide-base, des radicaux libres, etc.

Les titres de chapitres suivants complètent ce bref aperçu du domaine traité:
L'indice de liaison et sa signification physico-chimique (58 p.)
Distribution des charges électriques et moments dipolaires (58 p.)
Spectres électroniques, couleurs (78 p.)
Le diamagnétisme des composés aromatiques (24 p.)
Diagramme moléculaire et réactivité chimique (80 p.)

En résumé, c'est un ouvrage dont les premières pages étonneront peut-être le chimiste par un appareillage mathématique quelque peu inhabituel, mais qui, une fois ce léger obstacle surmonté, lui ouvrira des horizons extraordinairement vastes sur les problèmes si complexes de la Chimie Théorique.

G. BARBEZAT (Genève)

Acid-Base Titrations in Nonaqueous Solvents, par JAMES S. FRITZ, Ph. D., The G. Frederick Smith Chemical Company, Columbus, Ohio 1952, 47 pages (59 références)

Dans cette monographie, l'auteur passe en revue les possibilités actuelles de titration en milieux non aqueux. Si la méthode est encore relativement peu étudiée, elle est susceptible de très larges applications, pour peu que les principes généraux en soient établis et que certaines recherches théoriques soient entreprises.

Suivant le plan de l'ouvrage, nous trouvons d'abord un bref rappel des théories acide-base, puis leur extension à des solvants autres que l'eau. Deux grandes parties traitent ensuite de la titration des bases et des acides, les points suivants étant mis en évidence dans les 2 cas:
Solvants et réactifs,
Indicateurs ou électrodes indicatrices
Méthodes diverses
Interférence, Précision.

Des exemples de titrations d'acides aminés, amines, sels, etc. pour les bases, et d'acides carboxyliques, énols, imides, sulfonamides, phénols, pyrroles, alcools, pour les acides, complètent l'ouvrage.

G. BARBEZAT (Genève)

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COPPER(II)-DITHIZONE EQUILIBRIA IN WATER-CARBON TETRACHLORIDE

by

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The following equilibria are among those involved in the extraction of copper (II) from a water solution (*w*) by dithizone (diphenylthiocarbazone), H_2Dz, in an immiscible organic solvent (*o*):

$$\underset{w}{H_2Dz} \rightleftharpoons \underset{o}{H_2Dz} \qquad [H_2Dz]_o/[H_2Dz]_w = P_{dz} \qquad (1)$$

$$\underset{w}{H_2Dz} \rightleftharpoons H^+ + HDz^- \qquad [H^+][HDz^-]/[H_2Dz]_w = K_1 \qquad (2)$$

$$HDz^- \rightleftharpoons H^+ + Dz^{-2} \qquad [H^+][Dz^{-2}]/[HDz^-] = K_2 \qquad (3)$$

$$\underset{w}{Cu(HDz)_2} \rightleftharpoons \underset{o}{Cu(HDz)_2} \qquad [Cu(HDz)_2]_o/[Cu(HDz)_2]_w = P_p \qquad (4)$$

(primary Cu dithizonate)

$$\underset{w}{Cu(HDz)_2} \rightleftharpoons Cu^{+2} + 2HDz^- \qquad [Cu^{+2}][HDz^-]^2/[Cu(HDz)_2]_w = K_p \qquad (5)$$

$$\underset{w}{CuDz} \rightleftharpoons \underset{o}{CuDz} \qquad [CuDz]_o/[CuDz]_w = P_s \qquad (6)$$

(secondary Cu dithizonate)

$$CuDz \rightleftharpoons Cu^{+2} + Dz^{-2} \qquad [Cu^{+2}][Dz^{-2}]/[CuDz]_w = K_s \qquad (7)$$

$$Cu^{+2} + 2\underset{o}{H_2Dz} \rightleftharpoons \underset{o}{Cu(HDz)_2} + 2H^+ \qquad \frac{[Cu(HDz)_2]_o[H^+]^2}{[Cu^{+2}][H_2Dz]_o^2} = (K_p)_{ext.} \qquad (8)$$

$$Cu^{+2} + \underset{o}{H_2Dz} \rightleftharpoons \underset{o}{CuDz} + 2H^+ \qquad \frac{[CuDz]_o[H^+]^2}{[Cu^{+2}][H_2Dz]_o} = (K_s)_{ext.} \qquad (9)$$

$$\underset{o}{Cu(HDz)_2} + Cu^{+2} \rightleftharpoons \underset{o}{2CuDz} + 2H^+ \qquad \frac{[CuDz]_o^2[H^+]^2}{[Cu(HDz)_2]_o[Cu^{+2}]} = K_{ps} \qquad (10)$$

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* From the Ph. D. thesis of R. W. GEIGER, University of Minnesota, 1951. Present address, Works Laboratory, General Electric Company, Fort Wayne, Indiana.

The first seven of these are the fundamental equilibria and with the values of the corresponding constants known, the distribution of copper in its three forms between the two phases can be predicted for given values of $[H^+]$ and dithizone concentration. These constants are difficult to determine accurately because of the extremely low solubility of dithizone and the copper dithizonates in water. The constants of (8), (9), and (10), which are of practical importance, can be determined more easily.

In the present work, constants (4), (6), and (10) have been determined with carbon tetrachloride as the immiscible solvent. Values for (8) have already been reported, but this constant has been redetermined for various ionic strengths in perchlorate and chloride media. By the use of alcoholic solutions, values have been obtained for (2) and (5). The secondary ionization constant of dithizone, (3), remains undetermined but an upper limit has been assigned to it.

APPARATUS

A Beckman model B spectrophotometer with 1 cm glass cells was used in photometric measurements.

Solutions were shaken in a mechanical shaker at 300 cycles per minute. The arm had a length of 29 cm and moved through an arc of 15°.

MATERIALS

Water, alcohol and hydrochloric acid were re-distilled from an all-Pyrex apparatus. Ammonium hydroxide was obtained by isothermal distillation in a desiccator; the ammonia was absorbed in metal-free water in a silica dish.

Carbon tetrachloride. Reagent-grade carbon tetrachloride of various manufacturers contains variable amounts of a substance inhibiting the reaction between cupric ion and dithizone in acid medium. The nature of this impurity has not been established but it may be a sulfhydryl compound. Various methods of purification were tried. The following procedure was found to provide a product which gave dithizone solutions reacting rapidly with copper and which were stable on standing. One litre of reagent-grade carbon tetrachloride was treated with a few drops of liquid bromine and allowed to stand at least two weeks. It was then refluxed 4 hours with 10% sodium hydroxide, washed with water to remove the alkali, and shaken for 5 minutes with 10% hydroxylamine hydrochloride solution. The product was distilled after washing with water and drying with "drierite".

Perchloric acid and sodium perchlorate. Oxidizing agents and any traces of dithizone-reacting metals were removed from $1M$ perchloric acid by shaking for a day with a strong solution of dithizone in carbon tetrachloride. A $5M$ solution of sodium perchlorate was prepared by neutralizing 70% perchloric acid with sodium hydroxide solution with ice-bath cooling. Oxidizing impurities and heavy metals in the solution were removed by shaking with dithizone in carbon tetrachloride.

Sodium chloride and buffers (*Clark-Lubs*). Solutions of these were purified by shaking with dithizone.

Copper chloride and perchlorate. Stock solutions were standardized iodometrically and suitably diluted. The copper perchlorate solution was obtained by adding a slight excess of dilute perchloric acid to basic copper carbonate.

Dithizone. A filtered solution of one-half gram of Eastman dithizone in 50 ml of chloroform was shaken with four 50 ml portions of 1:100 metal-free ammonium hydroxide, and sulfur dioxide was bubbled into the ammoniacal extracts to precipitate dithizone. The solid was extracted with three 20 ml-portions of chloroform; the extracts were washed with water, and finally treated at ice-bath temperature with an equal volume of carbon tetrachloride. The precipitate was collected in a sintered-glass crucible and dried over magnesium perchlorate. The dithizone content of the product, as determined by extractive titration with standard silver solution, varied from 97 to 99% in different batches. The deficit is probably largely accounted for by the presence of water. The molar extinction coefficients of dithizone in carbon tetrachloride at 25° were found to be 19,800 at 450 mμ (absorption maximum), 5070 at 510 mμ (minimum), and 31,000 at 620 mμ. These values are slightly greater than those reported by other workers.

Primary copper dithizonate. The solid was required for the determination of solubility in carbon tetrachloride. It was prepared by shaking 100 ml of a 1% (weight/volume) dithizone solution in chloroform with a 5% excess of copper ion in 0.01*N* hydrochloric acid, filtering the chloroform extract, and adding twice its volume of carbon tetrachloride to precipitate the primary dithizonate. It was washed with carbon tetrachloride and dried in air and finally over magnesium perchlorate. The copper content (by iodometric titration) was 10.6% (theoretical 11.1%). The deficiency in copper is probably largely due to the presence of water. The molar extinction coefficient curve of the solid in carbon tetrachloride was identical with that of a solution obtained by shaking a dithizone solution of known concentration with a slight excess of copper in weakly acid medium, except below 450 mμ, where the solution of the solid gave very slightly lower values. The molar extinction coefficient of primary cupric dithizonate in carbon tetrachloride at 545 mμ, the wave length of maximum absorption, was found to be $4.5 \cdot 10^4$ ($\pm$ $0.05 \cdot 10^4$), based on the conversion of dithizone of known strength into the copper dithizonate.

Secondary copper dithizonate. Fifty ml of chloroform containing 0.5 g dithizone was shaken with 100 ml of 1*M* copper chloride (pH 6) for 30 minutes. The chloroform layer was separated and nitrogen was bubbled through until its volume had been reduced to 5 ml. The separated solid was filtered off, and dried in air and then over magnesium perchlorate. The copper content of the product was 19.4% (theoretical 20.0% for secondary cupric dithizonate). The molar extinction curves based on the solid dissolved in carbon tetrachloride and on dithizone transformed into the secondary copper dithizonate with excess copper agreed excellently. The molar extinction coefficient in carbon tetrachloride at 25° is $2.27 \cdot 10^4$ ($\pm 0.03 \cdot 10^4$) at 455 mμ, the wave length of maximum absorption.

EXPERIMENTAL

Solubility of dithizone in ethyl alcohol-water mixtures. From photometric measurements of saturated solutions ($0.01 M$ in hydrochloric acid), the following solubility values were found at 25°:

Per cent. C_2H_5OH by volume	35	50	70	90
Molar solubility $\times 10^5$	0.6	2.8	12.0	46

The extinction of the solutions was measured at 590 mμ, and the calculations were based on extinction coefficients determined for each alcohol concentration. The color of alcoholic dithizone solutions ranges from green at 100%, through blue in 50%, to blue-violet in 10% alcohol.

Below 30% alcohol concentration the saturated solutions are too weakly colored to be measured successfully in a 1 cm cell. Extrapolation shows that the molar solubility of dithizone in water is very probably not more than $2 \cdot 10^{-7}$ and may approximate $1 \cdot 10^{-7}$. The latter value is uncertain because of the long range extrapolation required. By a partition method the solubility $2 \cdot 10^{-7} M$ has already been found for water saturated with carbon tetrachloride[1]. A solubility of $8 \cdot 10^{-4} M$ in 100% ethyl alcohol is obtained by extrapolation of the above figures.

Primary ionization constant of dithizone. Although this constant has already been obtained from partition measurements[1,2,3], it seemed desirable to determine it from spectrophotometric measurements of the concentration of the ionized and un-ionized forms in ethyl alcohol-water mixtures. (After the present work had been completed, DYRSSEN AND HÖK[4] reported values for the ionization constant based on the molecular solubility of dithizone in water as determined with radioactive silver). The solubility of dithizone in dilute alcohol solutions is very small but it is possible to obtain supersaturated solutions, which, if the electrolyte concentration is not too high, remain stable long enough for the photometric measurements to be made.

The ratio of $[HDz^-]$ to $[H_2Dz]_w$ was obtained by measuring the transmittancy of the buffered solution (∼pH5) at 590 mμ and calculating the concentrations of the two species from the known extinction coefficients. At this wave length the molar extinction coefficient of HDz^- in alcoholic solutions is less than 1000, whereas that of H_2Dz is greater than 40,000 in the range of alcohol concentrations used. The total concentration of dithizone ranged from 4 to $8 \cdot 10^{-6} M$. The hydrogen ion activity was obtained by the use of a glass electrode. In one series of experiments the ionic strength was adjusted to 0.1M and in another to 1M with sodium perchlorate. The former series gave values for the ionization constant showing a regular variation with alcohol concentration (Fig. 1). At 1M ionic strength difficulty was encountered from the salting-out of dithizone, and the values are irregular:

C_2H_5OH, % by volume	10	15	20	30	40
$K_1' = ([HDz^-]/[H_2Dz]_w)\,aH^+$, $\times 10^5 (25°)$	1.8	1.6	1.2	2.4	1.5

Secondary ionization constant of dithizone. The transmission curve of dithizone in 1.5M sodium hydroxide is not significantly different from that in 0.1M or weaker solutions. In strong potassium hydroxide solution ($\sim$10M) a color change toward red-violet occurs, which may be due to Dz^{-2}. The potassium hydroxide used contained relatively much silver, but cyanide was added on the assumption that it would complex the silver and prevent its reaction with dithizone. Because of this and other complications an actual determination of the secondary ionization constant was not carried out, but it is judged from the observations made that its value is less than 10^{-15}.

The ratio K_p/K_1^2. This quantity, $[Cu^{+2}]\,[H_2Dz]_w^2/[Cu(HDz)_2]_w[H^+]^2$, was determined at various alcohol concentrations. In order to produce a measurable amount of dissociation of $Cu(HDz)_2$ it is necessary to acidify the solutions to about 1M. Because of the low solubility of the dithizonate in dilute alcoholic solutions and the salting-out effect of the electrolyte, only an approximate value of the ratio could be obtained. The determination was carried out by adding a $10^{-5}M$ solution of dithizone in absolute ethyl alcohol to an alcoholic mixture of copper ion in known amount (roughly equivalent to the dithizone) and perchloric acid. The solution was mixed for one-half minute and the transmittancy was immediately determined at 590 mμ. Since the transmission decreased on standing, the transmittancy readings were repeated at minute intervals for 8 minutes and the value for zero time was obtained by back-extrapolation of the extinction values (linear relation). The molar extinction coefficient of primary copper dithizonate used in the calculations is 30,000 ($\pm$2%) at 590 mμ. This figure is based on measurements in 50, 60, 70 and 80% alcohol, in which range it is constant. In 40% and weaker, slightly acidic, alcohol solutions reasonably accurate values for the extinction coefficient could not be obtained.

Spectrophotometric measurement gave the values of $[Cu(HDz)_2]_w$ and $[H_2Dz]_w$, and $[Cu^{+2}]$ was found by difference from the known total amount of copper present. The hydrogen ion concentration was obtained from the volume and concentration of the added acid. Table I gives the values of K_p/K_1^2.

Carbon tetrachloride-water partition coefficients of primary and secondary copper dithizonates. The partition coefficient of the primary dithizonate was determined

TABLE I

K_p/K_1^2 IN ETHYL ALCOHOL-WATER

C_2H_5OH, % by volume	40	30	20	0
K_p/K_1^2 ($1M$ Cl^-), 25°	$9\cdot10^{-12}$	$3\cdot10^{-12}$	$17\cdot10^{-13}$	10^{-14}[a]

[a] By extrapolation. The corresponding value of K_p is $\sim 1\cdot10^{-23}$ if K_1 is taken equal to $3\cdot10^{-5}$, the value at $0.1M$ ionic strength.

at 25° by vigorously shaking 25 ml of $1.3\cdot10^{-3}M$ dithizone in carbon tetrachloride with 800 ml of water acidified to pH 0.75 to 2 with hydrochloric acid and containing excess copper ion ($3\cdot10^{-4}$ to $7\cdot10^{-4}M$), extracting $Cu(HDz)_2$ from 500 ml of the filtered aqueous phase by brief shaking with 5 ml carbon tetrachloride, and obtaining the transmittancy of the extract at 555 mμ. The initial shaking time varied from 30 to 120 minutes. The values of $[Cu(HDz)_2]_{CCl_4}/[Cu(HDz)_2]_w$ ranged from 6.0 to $8.2\cdot10^4$ in 8 determinations, with an average of $7.3\cdot10^4$, which may as well be rounded off to $7\cdot10^4$. The extinction curve of the extract showed that no important amount of secondary copper dithizonate was present. From the value of the constant for the equilibrium between primary and secondary copper dithizonate, it would be expected that a large fraction of the copper would be present as the secondary dithizonate in the final carbon tetrachloride extract. This is not the case, however, because of the slowness of attainment of this equilibrium.

For the determination of the partition coefficient of the secondary dithizonate, 25 ml of $1.3\cdot10^{-3}M$ dithizone in carbon tetrachloride was shaken for 1 to 2 hours with 800 ml aqueous solution of pH $\sim$6 containing a hundred-fold excess (3.5 millimoles) of copper ion. The filtered aqueous solution was extracted with a small volume of carbon tetrachloride and the transmittancy of the extract

TABLE II

PARTITION COEFFICIENTS AND SOLUBILITIES OF COPPER DITHIZONATES AND DITHIZONE (25°)

	P_{CCl_4/H_2O}	Soly. in CCl_4 M	Soly. in H_2O[a] M
$Cu(HDz)_2$	$7\cdot10^4$	$5.5\cdot10^{-4}$	8.10^{-9}
CuDz	$2\cdot10^4$	$\lesssim 1\cdot10^{-3}$	$\lesssim 6\cdot10^{-8}$
H_2Dz[b]	$1.1\cdot10^4$	$2.1\cdot10^{-3}$	$2\cdot10^{-7}$[c]

a Calculated from P and soly. in CCl_4
b From SANDELL[1]
c DYRSSEN AND HÖK[4] report $2.5\cdot10^{-7}$ for the molar solubility in $0.1M$ perchloric acid, based on a radioactive method.

determined at 455 mμ. Nine determinations gave values ranging from 1.5 to $2.5 \cdot 10^4$, with an average of $2.0 \cdot 10^4$ for $[CuDz]_{CCl_4}/[CuDz]_w$ at 25°.

The partition coefficient for dithizone between carbon tetrachloride and water at 25° has been reported[1] as $1.1 \cdot 10^4$. This value was verified in the present work, a number of experiments giving ratios of 1.0 to $1.2 \cdot 10^4$ at 25°.

Solubility of copper dithizonates in carbon tetrachloride. In the determination of the solubility of the primary dithizonate, 20 to 30 mg of the solid was shaken for 15 to 400 minutes with 2 ml of carbon tetrachloride in a nitrogen atmosphere. After pressure filtration through a sintered-glass disc, the transmittancy of the filtrate, suitably diluted with carbon tetrachloride, was determined at 550 mμ. Six experiments gave values from 5.48 to $5.61 \cdot 10^{-4}M$, average $5.5 \cdot 10^{-4}M$ (25°).

The solubility of the secondary dithizonate was determined similarly; the concentration of the filtered solution was obtained from transmittancy readings at 455 mμ. Only an approximate figure for the solubility could be obtained, because even after vigorous shaking for 3 hours the system had not come to equilibrium. After 3-hour shaking the apparent solubility was about one-half that after 0.5-hour shaking. The decrease may be due to growth of very fine particles to coarser ones. The transmission curve of a solution shaken for 3 hours was normal. The lowest apparent solubility found (3-hour shaking) was $1.2 \cdot 10^{-3}M$, which is considered to be the upper limit of the solubility at 25°.

Equilibrium constant for carbon tetrachloride extraction of primary copper dithizonate. From 5 to 20 ml of a carbon tetrachloride solution of dithizone (4 to $10 \cdot 10^{-5}M$) was shaken in a glass-capped bottle under nitrogen with 20 to 150 ml of aqueous copper solution (7 to 25 γ Cu^{+2}) containing hydrochloric or perchloric acid together with sodium chloride or perchlorate to keep the ionic strength

TABLE III

EQUILIBRIUM CONSTANT FOR CARBON TETRACHLORIDE EXTRACTION OF PRIMARY COPPER DITHIZONATE AT 25°

Ionic strength M	$[H^+]$ M	$(K_p)_{ext.}$ $\times 10^{-10}$	No. of Measurements	Average deviation of single measurement, % relative
1.00 (Cl^-)	1.00	1.1	4	10
1.00 (Cl^-)	0.80	1.0	4	10
1.00 (Cl^-)	0.50	1.0	7	10
1.00 (Cl^-)	0.25	0.9	4	10
2.00 (Cl^-)	2.00	0.69	7	5
3.1 (Cl^-)	3.1	0.32	3	5
1.0 (Cl^-)	1.0	1.6[a]	3	5
1.15 (ClO_4^-)	1.15	1.5	7	7
0.6 (ClO_4^-)	0.6	1.9	4	5

[a] Carbon tetrachloride solution of copper dithizonate shaken with acid aqueous solution.

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constant. The solutions were shaken for various lengths of time in each series to check attainment of equilibrium. Two or three minutes of shaking under the conditions mentioned was ample.

The concentration of $Cu(HDz)_2$ in the carbon tetrachloride phase was found by reading the transmittancy at 535 mμ and making use of a suitable calibration curve. The final dithizone concentration in the carbon tetrachloride and the copper concentration in the aqueous phase were obtained by difference, from the known amounts taken. The relative volumes of the two phases were so chosen that the amounts of copper in the two were not too disproportionate, else the accuracy suffers. Blanks were run on the reagents to correct for any small amounts of copper present. The hydrogen-ion concentration was found by titration. See Table III for the values of the constant.

Primary-secondary copper dithizonate equilibrium constant. Five ml of 3 to $4 \cdot 10^{-5} M$ dithizone in carbon tetrachloride was shaken with 25 ml of $4 \cdot 10^{-4}$ to $1 \cdot 10^{-2} M$ copper solution at pH 2.8 to 1.4 and the concentration of the two dithizonates in the carbon tetrachloride was found by transmission readings at 550 mμ, with confirmatory readings at 445 mμ. Equilibrium is reached slowly and the mixtures were shaken for 20-60 minutes in a nitrogen atmosphere at 300 cycles per minute. The pH was measured with a glass electrode. The results are reported in Table IV.

It was observed in these experiments that the primary copper dithizonate was formed first and that it was transformed into the secondary dithizonate on continued shaking.

DISCUSSION

The present values of $(K_p)_{\text{ext.}}$ ($1.0 \cdot 10^{10}$ in $1M$ chloride and $1.5 \cdot 10^{10}$ in $1.15M$ perchlorate medium) may be compared with ANONSEN's[5] value of $2 \cdot 10^{10}$ for $1M$ chloride and KOROLEFF's[6] average of $3.4 \cdot 10^{10}$ for 0.6—$6M$ sulfate at room temperature. Little complexing of copper by chloride in $1M$ Cl^- solution is indicated. From the value $1.9 \cdot 10^{10}$ in $0.6M$ perchlorate, $(K_p)_{\text{ext.}}$ in $0.1M$ perchlorate medium may be estimated as $3 \cdot 10^{10}$.

TABLE IV

PRIMARY-SECONDARY COPPER DITHIZONATE EQUILIBRIUM CONSTANT IN CARBON TETRACHLORIDE-WATER

Ionic strength (NaCl) M	pH	$K_{ps} = \dfrac{[CuDz]_o^2\ (aH^+)^2}{[Cu(HDz)_2]_o[Cu^{+2}]} \times 10^6$
0.1	2.0	2.0
0.1	1.4	2.4
0.01	2.0	5.6
0.002	2.75	6.9

The copper-dithizone extraction reaction is reversible as shown by one of the experiments in Table III, in which a carbon tetrachloride solution of primary copper dithizonate was shaken with 1M hydrochloric acid. Considering the experimental errors involved, the value of K thus obtained, $1.6 \cdot 10^{10}$, is not significantly different from that obtained by approaching equilibrium in the other direction. The rates of attainment of equilibrium from the two sides are comparable.

A rough estimate of $(K_p)_{\text{ext.}}$ can be obtained from its component constants:

$$(K_p)_{\text{ext.}} = P_p K_1^2 / K_p P_{dz}^2 \qquad \text{(from equations 1,2,4,5,8)}$$

Because of the low solubility of $Cu(HDz)_2$ in dilute alcohol solutions, precise values of K_p/K_1^2 have not been obtained. Extrapolation of the figures for this ratio in Table I indicates that in water its value probably lies within the limits $1 \cdot 10^{-13}$ and $7 \cdot 10^{-15}$. The corresponding limits of $(K_p)_{\text{ext.}}$ are then $6 \cdot 10^9$ and $8 \cdot 10^{10}$, within which the directly determined value is found to lie. The directly determined value of K_p, the ionization constant of primary copper dithizonate in water, is $\sim 1 \cdot 10^{-23}$. A more accurate value can be obtained indirectly from $(K_p)_{\text{ext.}}$ and K_1. Taking $(K_p)_{\text{ext.}}$ and K_1 to be respectively $3 \cdot 10^{10}$ and $3 \cdot 10^{-5}$ at 0.1M ionic strength, K_p is found to be $2 \cdot 10^{-23}$.

No indication has been obtained of the presence of appreciable amounts of an intermediate ion such as $Cu(HDz)^+$.

The following expression can be derived for the constant of the equilibrium between primary and secondary copper dithizonates in carbon tetrachloride:

$$(K_{ps})_o = \frac{[CuDz]_o [H_2Dz]_o}{[Cu(HDz)_2]_o} = (K_p)_{\text{ext.}}^{-1/2} K_{ps}^{1/2} = 1 \cdot 10^{-5} \cdot 1.5 \cdot 10^{-3} = 1 \cdot 10^{-8}$$

(The value is somewhat approximate, because the value of $(K_p)_{\text{ext.}}^{-1/2}$ is for 1M chloride medium, that of $K_{ps}^{1/2}$ for 0.1M chloride, and the partition coefficients of the three species between carbon tetrachloride and water have been assumed the same for 1 as for 0.1M ionic strength). The magnitude of this constant shows that dilute solutions of primary copper dithizonate in carbon tetrachloride are appreciably dissociated into the secondary dithizonate and free dithizone. Thus a $10^{-5}M$ solution of $Cu(HDz)_2$ will be dissociated approximately 3 per cent. This dissociation needs to be taken into account in obtaining extinction coefficients and extinction curves of the primary dithizonate.

From the constants given, various others can be obtained, such as the Cu^{+2}-H_2Dz equilibrium constant in water, the solubility product of primary copper dithizonate, etc. The extraction constant for secondary copper dithizonate is

$$(K_s)_{\text{ext.}} = (K_p)_{\text{ext.}}^{1/2} \, (K_{ps})^{1/2} = (3 \cdot 10^{10} \cdot 2 \cdot 10^{-6})^{1/2} = \sim 2 \cdot 10^2 (0.1M \text{ ionic strength}).$$

By linear extrapolation of pK_1 in alcohol solutions (Fig. 1), a value of $2.8 \cdot 10^{-5}$ is found for K_1 of dithizone in water at an ionic strength of 0.1*M*. This figure is considerably higher than that ($1.5 \cdot 10^{-5}$) obtained by one of us from partition experiments[1]. The difference is larger than would be expected from the errors in either method. The present value may be slightly higher than the true value because, in analogy with other weak acids in alcohol, the curve in the figure may show an upward curvature near the pK_1 axis. At the worst, however, this could not decrease K_1 below $2 \cdot 10^{-5}$. The present value agrees very well with that reported by DYRSSEN AND HÖK[4]. From their value of 4.46 for pK_1 based on hydrogen ion concentration, the value $2.6 \cdot 10^{-5}$ for K_1 based on hydrogen ion activity at 0.1*M* ionic strength may be calculated. IRVING AND BELL'S[3] revised value for pK_1 is 4.5 ± 0.3.

Analytical bearing of results. The question of the completeness of extraction of copper from mineral acid solutions is of particular importance. When copper is to be determined in a sample of more or less complex composition it is frequently necessary to isolate it first by extracting with a 0.01% weight/volume ($4 \cdot 10^{-4}M$) solution of dithizone. It is generally desirable to keep the acidity high to reduce the extraction of other reacting metals such as zinc. If we require the extraction of copper to be 99.9% complete from 1*M* hydrochloric acid, the concentration of

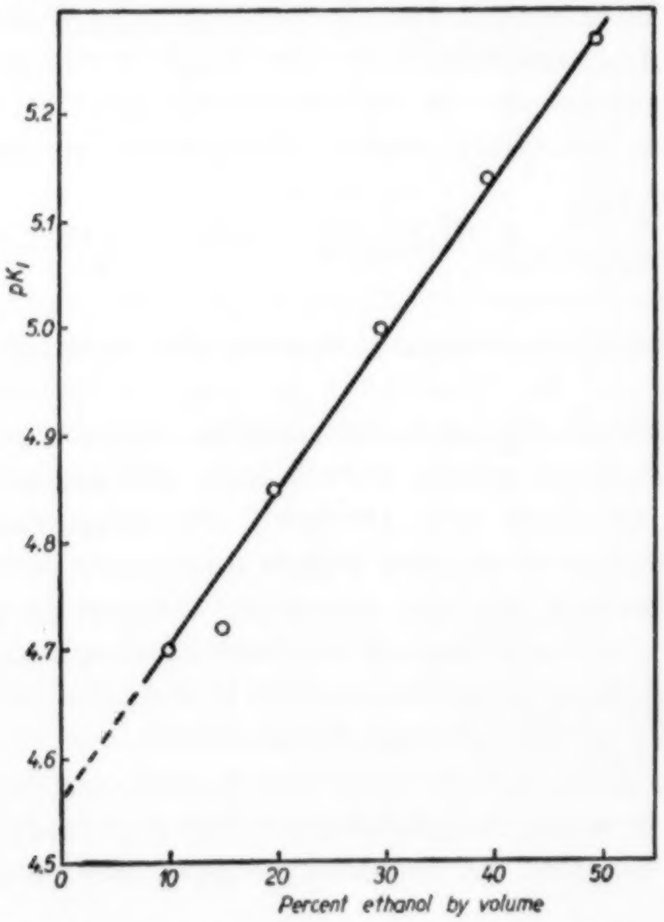

Fig. 1. pK_1 of dithizone in ethanol-water at 0.1 *M* ionic strength (25°). Each point is the average of 3 to 6 determinations.

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dithizone in the carbon tetrachloride phase at equilibrium must be approximately $3 \cdot 10^{-4} M$ (the two phases being assumed equal in volume) as follows from:

$$\frac{[H_2Dz]_o^2}{[H^+]^2} = \frac{[Cu(HDz)_2]_o}{[Cu^{+2}]} \times \frac{1}{1 \cdot 10^{10}} = \frac{1000}{10^{10}} = 10^{-7}$$

$$[H_2Dz]_o = \sqrt{10^{-7}} = 3 \cdot 10^{-4}\, M$$

This figure shows that copper can be extracted quantitatively from $1M$ mineral acid medium with 0.01% dithizone solution in carbon tetrachloride by shaking with successive portions of the latter until the last portion remains essentially unchanged in color.

In the final determination of copper by the mixed color method, a 0.001% weight/volume solution of dithizone in carbon tetrachloride is commonly used. Here the acidity of the solution should not exceed $0.1M$. For 99.9% extraction of copper from an aqueous solution of this acidity the final concentration of dithizone in the carbon tetrachloride must be $3 \cdot 10^{-5}\, M$, and for 99% extraction it must be $1 \cdot 10^{-5}\, M$. In the absence of reacting metals an acidity of $0.01M$ is somewhat preferable. The use of buffer solutions as recommended by some is not necessary. The rate of reaction of copper with dithizone is not strongly dependent upon the acidity, being only 3 or 4 times as great in $0.01M$ as in $1M$ hydrochloric acid.

There is no danger of the formation of secondary copper dithizonate in the mixed color method. In order that 99% of the copper be present as the primary dithizonate, the concentration of free dithizone in the carbon tetrachloride phase at equilibrium need be only

$$[H_2Dz]_o = 100 \times (K_{ps})_o = \sim 1 \cdot 10^{-6}\, M.$$

This figure also shows that the mono-color method (in which excess dithizone is removed from the carbon tetrachloride solution of copper dithizonate by shaking with an alkaline aqueous solution) can not well be accurate. It is true that the equilibrium between the primary and secondary dithizonates is established rather slowly, but nevertheless the method should be avoided, at least in accurate work.

SUMMARY

Values are reported for the partition coefficients of primary and secondary cupric dithizonates, the equilibrium constants for the extraction of the dithizonates, and the primary-secondary copper dithizonate equilibrium constant, all for water-carbon tetrachloride. The primary ionization constant of dithizone in ethyl alcohol-water mixtures has been determined. Carbon tetrachloride solutions of primary copper dithizonate are shown to be dissociated to some extent into the secondary dithizonate and free dithizone. The analytical significance of the results is discussed.

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RÉSUMÉ

Les valeurs suivantes ont été déterminées: coefficients de partage des dithizonates de cuivre primaire et secondaire, constantes d'équilibre pour l'extraction des dithizonates et constantes d'équilibre du dithizonate de cuivre primaire et secondaire, dans le milieu eau-tétrachlorure de carbone. Il a été déterminé également la constante d'ionisation primaire de la dithizone dans les mélanges alcool éthylique - eau. Le dithizonate de cuivre primaire en solution dans le tétrachlorure de carbone, est dissocié en dithizonate secondaire et dithizone libre. Ces résultats envisagés du point de vue analytique sont discutés.

ZUSAMMENFASSUNG

Es werden Werte berichtet für die Verteilungskoeffizienten von primären und sekundären Kupfer-II-dithizonat, die Gleichgewichtskonstanten für die Dithizonatextraktion und die Gleichgewichtskonstante für primäres und sekundäres Kupfer-II-dithizonat, alle für das System Wasser-Tetrachlorkohlenstoff. Die primäre Dissoziationskonstante von Dithizon in Äthylalkohol-Wassermischungen wurde bestimmt. Es wurde gezeigt, dass die Lösungen von primären Kupferdithizon in Tetrachlormethan teilweise in sekundäres Dithizonat und freies Dithizon dissoziiert sind. Die analytische Bedeutung dieser Ergebnisse wird besprochen.

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2,4,6-TRINITROBENZOIC ACID AS A PRIMARY STANDARD IN ACIDIMETRY

by

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INTRODUCTION

Primary standards employed in acidimetry are represented by a comparatively large group of available chemical compounds. Both solid and liquid reagents are included. Organic and inorganic compounds are available both hydrated and anhydrous. The range of equivalent weights varies from less than 60 to nearly 300. The acids represented are preferably monobasic and the most popular type are strong acids (pK_a approximately 2 or less) although weak acids are also serviceable.

The most desirable preference is that which favors crystalline reagents as distinct from liquids, strong acids as compared to weak acids, high as compared to low equivalent weights and anhydrous as choice in place of hydrated materials. A tabulation of the most common primary standards in acidimetry and pertinent data for each reagent is given in Table I. These standards have been selected as preferred reagents by text books in general of quantitative analysis.

Constant boiling hydrochloric acid[1] is accepted as the ultimate standard acid. If the exact directions are followed for its preparation, both as to strict duplication of distillation apparatus design and the rate of distillation, the exact available hydrogen ion value is known with a precision comparable to atomic weight determination accuracy. Both oxonium perchlorate[5] and sulfamic acid[3] have been evaluated by direct comparison with this ultimate standard.

The United States Bureau of Standards issues a standard potassium acid phthalate (Standard Sample 84) which is accompanied by a "certificate of analysis" and a value for its effective neutralizing power. This sample is accepted as a convenient "secondary" ultimate standard of reference in acidimetry. Potassium acid phthalate has been used as standard of comparison in the present investigation.

Organic reagents which have been investigated as standards in acidimetry have been reviewed by WELCHER and the following acids cited:

TABLE I

COMMONLY PREFERRED PRIMARY STANDARDS IN ACIDIMETRY AND DESCRIPTIVE QUALIFICATION DATA

Reagent	Formula	Equivalent Weight	Acid Type	Literature Reference
Hydrochloric Acid (Const. Boiling)	HCl	36.46	Strong	(1)
Oxalic Acid	$H_2C_2O_4.2H_2O$	53.03	pK_{a_2} 4.3	(2)
Sulfamic Acid	HSO_3NH_2	97.10	pK_a 2.0	(3)
Benzoic Acid	C_6H_5COOH	122.12	pK_a 4.2	(4)
Dioxonium Perchlorate ($HClO_4.2H_2O$)	$O_2H_5ClO_4$	126.50	Strong	(5)
Potassium Acid Phthalate	$KHC_8H_4O_4$	204.22	pK_{a_2} 5.4	(6)
Potassium Bi-Iodate	$KH(IO_3)_2$	389.94	pK_a 0.7	(7)

Aliphatic acids. Oxalic, adipic, malic, maleic, malonic, fumaric, succinic, and tartaric.

Aromatic acids. Benzoic, salicylic, *para*-nitrobenzoic, 2-nitro-4-sulfobenzoic, *ortho*-chlorobenzoic, picric, pseudocumene sulfonic and pyridinium perchlorate.

Amino acids. 4-Amino-2-sulfobenzoic.

Acid anhydrides. Phthalic, succinic.

Other types. Furoic acid, ascorbic acid.

Literature references to published data concerning the standard of reference acids listed by WELCHER[8] will be omitted in the interest of space conservation and the WELCHER treatise is recommended in substitution.

It is generally accepted that those organic compounds in the category of weak acids (potassium acid phthalate accepted) are of secondary importance as primary standards. Previous investigations of their value, as a matter of record, are of service as procedures in proof of purity of the acids represented.

THE NITROBENZOIC ACIDS

The substitution of nitro groups in benzoic acid increases their hydrogen ion availability as follows:

Benzoic acid with a pK_a value of 4.2 is increased to pK_a values of 3.42, 3.49 and 2.17 by nitro-group substitutions in the para-, meta-, and ortho-positioned groups respectively. It would naturally be predicted that multiple substitutions of nitro groups in the benzoic acid molecule would give to the modified reagent an enhanced hydrogen ion availability. The commercially obtainable 2,4,6-trinitrobenzoic acid was therefore chosen for investigation. It is the objective of this paper to justify its selection by experimentally determining its many desirable features as a primary standard in acidimetry. Among its sterling qualifications are the facts that it is a strong monobasic acid (pK_a 2.38), has a high equivalent weight 257.12, and may be easily prepared in pure form. In addition it is a crystalline solid, anhydrous and stable at 130° C or in air for weighing and upon storage. A unique advantage is the fact that it serves as its own indicator upon neutralization (color change from colorless to red at approximately pH = 8). The titration of an approximately 0.1 normal solution of 2,4,6-trinitrobenzoic acid employing approximately 0.1 normal sodium hydroxide is shown graphically in Fig. 1.

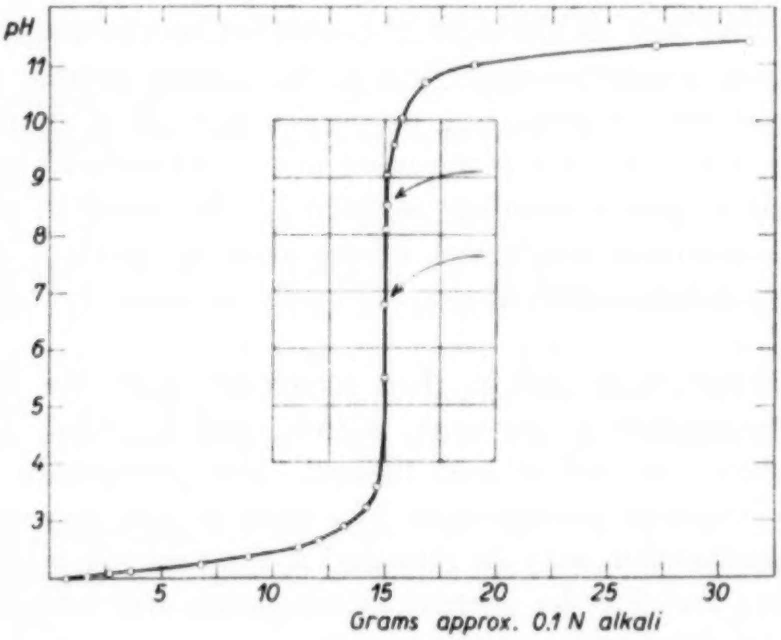

Fig. 1. The titration of 2,4,6-trinitrobenzoic acid by sodium hydroxide. Top arrow: self indicator equivalence point. Bottom arrow: bromthymol blue equivalence point.

From an examination of Fig. 1 it will be noted that the change in pH at the equivalence point is abrupt and covers the range pH 4.5 to pH 8.5 with a very small increment of alkali added. The self- indicating effect (at the point noted by the top arrow) occurs between a pH of 8.0 and 8.5. The lower arrow indicates the bromthymol blue equivalence point determination at the mid-point of the pH "break". This titration graph compares favorably to that given by BUTLER, SMITH AND AUDRIETH[3] for the corresponding titration of sulfamic acid and the pH "break" at the equivalence point is more pronounced. The approach to the equivalence point is gradual and gives ample indicator warning. The titration curve before and after the equivalence point "break" is exactly symmetrical.

PREPARATION OF REAGENT

Commercially available 2,4,6-trinitrobenzoic acid is prepared by the chromic-sulfuric acid oxidation of trinitrotoluene and the most prominent impurity present is the starting material. Purification involves the formation of the water soluble sodium salt, separation of trinitrotoluene by filtration and reconversion of the sodium salt to trinitrobenzoic acid by use of sulfuric acid followed by filtration and washing and drying.

A sample of 330 g of technical 2,4,6-trinitrobenzoic acid is suspended in 2000 ml of water at 35° C in a 4-litre beaker which is provided with an efficient motor stirrer. A solution of 15 per cent. sodium hydroxide is dropped in with continuous vigorous stirring. As fast as the acid is converted to the sodium salt it passes into solution. Upon complete conversion to the soluble sodium salt the solution will turn pink from its self-indicating properties at a pH of approximately 8.0 to 8.5. This precise neutralization point must not be exceeded and when attained the pH is lowered to give a colorless solution by the addition of a few drops of acetic acid. The insoluble impurities in the starting product are then filtered off and washed a few times with water. The insoluble impurity is chiefly trinitrotoluene.

The 2,4,6-trinitrobenzoic acid is then recovered from the filtrate. For this purpose a slight excess of 50 per cent. sulfuric acid is added. The solution and precipitated material is chilled and filtered. The precipitate is washed with cold water until free from sulfuric acid. The yield by this process is 60 per cent. The process of purification may be repeated if the starting material is shown to be of poor quality and for the present investigation this added precaution was applied "to make assurance doubly sure."

The crystals of 2,4,6-trinitrobenzoic acid are first dried in air, then in a desiccator over anhydrone, and finally in a drying oven at 85° C in preparation for examination as to purity by comparison with standard alkali. A drying temperature of 100° C was also applied as well as 130° C to prove stability of the test samples at these temperatures. This material may be ignited and ashed to prove the absence of non-volatile impurities. It is not sensitive to shock such as a blow by a hammer when placed on an anvil. By other tests it may be shown to be non-hazardous to store or handle.

PREPARATION AND STANDARDIZATION OF SODIUM HYDROXIDE

A sample of carbonate-free sodium hydroxide was dissolved in boiled distilled water. The volume of solution was approximately 10 l and the reaction samples were withdrawn from the stock solution into weight burets. Air to replace the volume of withdrawn reagent was passed successively through ascarite to remove carbon dioxide and then bubbled through a reservoir of the alkali solution to regulate its vapor pressure. All weighings of the titrating solution, the

TABLE II

THE STANDARDIZATION OF SODIUM HYDROXIDE USING POTASSIUM ACID PHTHALATE AS PRIMARY STANDARD

Wt. of $KHC_8H_4O_4$ taken for each titration = 0.2500^7 grams

Titration No.	1	2	3	4	5	Av.
Wt. NaOH Required	10.8770	10.8800	10.8870	10.8900	10.8868	10.8842

Av. Mil. Equivalents of primary standard per gram of NaOH = 0.11250

samples of crystalline standards of reference and the new reagent standard were corrected to the vacuum weight basis. The sodium hydroxide was approximately 0.1 volume normal.

The standardization of the sodium hydroxide solution employing U. S. Bureau of Standards Primary Standard potassium acid phthalate (Sample 84) was first applied. Weighed samples (identical weights for each sample) were dissolved in boiled distilled water in 400 ml beakers. These were stirred by use of an electromagnetic stirring apparatus and glass enclosed rotor. Phenolphthalein was employed as indicator. The results from a series of standardizations are given in Table II.

The same procedure employing pure[3] sulfamic acid was applied with the substitution of bromthymol blue as indicator for phenolphthalein. The results are given in Table III.

TABLE III

THE STANDARDIZATION OF SODIUM HYDROXIDE USING SULFAMIC ACID AS PRIMARY STANDARD

Wt. of HSO_3NH_2 taken for each titration = 0.3000^6 grams

Titration No.	1	2	3	4	5	Av.
Wt. NaOH Required	27.4883	27.4921	27.5014	27.4987	27.4967	27.4954

Av. Mil. Equivalents of primary standard per gram of NaOH = 0.11265

THE DETERMINATION OF 2,4,6-TRINITROBENZOIC ACID BY TITRATION EMPLOYING SODIUM HYDROXIDE

Pure 2,4,6-trinitrobenzoic acid prepared as previously described was dried at 85° C and 13 samples of 0.2000^5 grams were titrated by the standard sodium

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hydroxide using bromthymol blue as indicator. The calculated recovered weight of starting material was found to be from 0.0 to 0.3 mg per titration low with an average low value of 0.17 mg per titration or minus 0.085 per cent. The sample had probably not been freed from moisture by drying at 85°.

The same sample of 2,4,6-trinitrobenzoic acid was dried at 130° C for five hours and evaluated by comparison with standard sodium hydroxide with the results given in Table IV.

It will be observed from the data of Table IV that the determination of the purity of 2,4,6-trinitrobenzoic acid purified as described and dried at 130° C gave a satisfactory evidence of purity. The determinations showed a satisfactory degree of conformity and an average negative error of —0.014 per cent. was indicated.

TABLE IV

THE DETERMINATION OF 2,4,6-TRINITROBENZOIC ACID (DRYING TEMPERATURE = 130° C) BY TITRATION EMPLOYING STANDARD SODIUM HYDROXIDE

Indicator Bromthymol blue
Sample Wt. = 0.5001[1] grams

Sample No.	Wt. NaOH Sol'n Required g	2,4,6-Trinitrobenzoic Acid Found g	Error mg
1	17.2993	0.50017	+0.06
2	17.2913	0.49994	—0.17
3	17.2944	0.50003	—0.08
4	17.2982	0.50014	+0.03
5	17.2941	0.50002	—0.09
6	17.2924	0.49997	—0.14
7	17.2930	0.49999	—0.12
	Av. 17.2949	Av. 0.50004	Av. —0.07

Av. Mil. Equivalents of 2,4,6-trinitrobenzoic acid per gram of NaOH = 0.11247

CONCLUSIONS

Organic carboxylic acids, both of the aliphatic and aromatic type, have been proposed as primary standards in acidimetry in the case of an extensive series of investigations. Of these examples all, with few exceptions, are weak acids, (pK_a values more than 3 to 4) or are of low equivalent weight. The better selections are in the aromatic group and the most common preference is potassium acid phthalate, (Eq. Wt. 204.22, $pK_a = 5.4$). Primary standard acids should preferably be non-hydrated materials.

The selection of a new aromatic carboxylic acid for study as an improved primary standard calls for a strong acid with a high equivalent weight. The chosen material should preferably be a solid and in addition to these and other qualifications should be commercially available and be capable of purification by a simple, practical procedure. Two nitrated aromatic carboxylic acids which have the required pK_a values are *ortho*-nitrobenzoic acid ($pK_a = 2.19$), and 2,4,6-trinitrobenzoic acid ($pK_a = 2.38$). The latter was selected because of its higher equivalent weight (257.12), and because of its availability from the usual commercial sources. In addition, this new primary standard serves as a self-indicator, sodium 2,4,6-trinitrobenzoate, having a transition from colorless to red at approximately $pH = 8$. This property of the proposed new primary standard is of great advantage in the process of purification of technical grades of the starting material. Pure 2,4,6-trinitrobenzoic acid is obtained from impure stock by the process of formation of the sodium salt and reconversion to the parent substance after filtration to remove impurities, chiefly trinitrotoluene.

The purified samples of 2,4,6-trinitrobenzoic acid were found to be stable at a drying temperature of 130° C, are anhydrous and non-hygroscopic, easily water soluble and stable in storage. The sodium salt of this acid serves as a self-indicator but the theoretical equivalence point is denoted more precisely by the use of bromthymol blue as indicator. The proposed new primary standard was evaluated with high resulting precision by comparison with two accepted primary standards, sulfamic acid and potassium acid phthalate.

SUMMARY

The purification of commercially available 2,4,6-trinitrobenzoic acid has been described. The impure acid is suspended in water, converted to the sodium salt which is water-soluble, by the addition of sodium hydroxide, the insoluble impurities filtered off and the parent substance thrown out of solution by the addition of an equivalent amount of sulfuric acid. The purified product is filtered, washed with water, dried in air, then in contact with an efficient drying agent, and finally at 130° C. The pure product was then compared with two accepted primary standard acids, potassium acid phthalate and sulfamic acid. The new primary standard has an equivalent weight of 257.12, is anhydrous, non-hygroscopic, and serves as its own neutralization indicator, although the use of bromthymol blue gives a more correct determination of the exact equivalence point.

RÉSUMÉ

On décrit une méthode de purification de l'acide 2,4,6, - trinitrobenzoïque. L'acide à purifier est mis en suspension dans l'eau, converti en sel de sodium soluble, par addition d'hydroxyde de sodium. Les impuretés insolubles sont filtrées, puis on reforme l'acide trinitrobenzoïque par addition d'une quantité équivalente d'acide sulfurique.

Le produit ainsi purifié est filtré, lavé à l'eau, séché à l'air, puis en présence d'un déshydratant et finalement à 130° C. Le produit pur est ensuite comparé avec deux acides étalon, le phthalate acide de potassium et l'acide sulfamique. L'acide trinitrobenzoïque, de poids moléculaire 257.12, est anhydre, non hygroscopique et sert d'indicateur lors de ses propres titrations, bien que le bleu de bromothymol permette une détermination du virage plus nette.

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ZUSAMMENFASSUNG

Es wurde die Reinigung handelsüblicher 2,4,6 - Trinitrobenzoesäure beschrieben. Die rohe Säure wird in Wasser suspendiert, durch Hinzufügen von Natriumhydroxyd in das wasserlösliche Natriumsalz übergeführt, von unlöslichen Verunreinigungen abfiltriert und die Stammverbindung durch Hinzufügen einer äquivalenten Menge Schwefelsäure aus der Lösung ausgefällt.

Das gereinigte Produkt wird filtriert, mit Wasser gewaschen, erst an der Luft, dann in Kontakt mit einem wirksamen Trockenmittel und schliesslich bei 130° C getrocknet. Das gereinigte Produkt wurde dann mit zwei allgemein anerkannten-säure-Urtitersubstanzen, dem sauren Kaliumphthalat und der Sulfaminsäure verglichen. Die neue Urtitersubstanz hat ein Äquivalentgewicht von 257.12, ist wasserfrei, nicht hygroskopisch und dient als ihr eigener Neutralisationsindikator,obwohl die Benützung von Bromthymolblau eine bessere Bestimmung des genauen Äquivalenzpunktes ermöglicht.

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STANDARDIZATION OF TITANOUS CHLORIDE AND SULPHATE SOLUTIONS

by

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INTRODUCTION

There have been recent references in the literature[1, 2, 3] to the standardization of titanous solution by means of potassium dichromate. This has an obvious appeal, in that no intermediate reagent is required between the titanous solution and the standard substance, but during an investigation in this laboratory it became clear that there are objections to the use of potassium dichromate. Some observers, *e.g.* BREIT[4], have recognised that results using potassium dichromate may be high, although the cause of the error does not appear to have been appreciated. The present paper describes experiments performed to examine the nature of this error and its possible elimination.

EXPERIMENTAL

As shown by KOLTHOFF AND TOMICEK[5], iron is often present as impurity in titanous solutions and can lead to a false end-point when potassium dichromate is used as standard substance. Supplies of titanous chloride and titanous sulphate which have been tested in these laboratories contained iron in amounts varying from 0.005% for the chloride to 0.065% for the sulphate. The interference caused by these amounts of iron is shown in Tables I and II, respectively.

In order to compare direct and indirect standardizations in the absence of iron, experiments were carried out on iron-free reagents.

Preparation of iron-free titanous sulphate solution. Two methods were used, the first according to POLIDORI[6], and the second devised in this laboratory.

Method 1. Violet crystals of titanous chloride were precipitated from ice-cold commercial solution by passing dry hydrogen chloride through it to saturation. The saturated solution was stored in an ice chest for several days until no further

TABLE I

Titanous chloride solution 0.2 *N* (Fe = 0.005%)

Method of Standardizing	Factor	
	Solution 1	Solution 2
Against standard ferric ammonium sulphate solution	1.301	0.980
Against 0.2 *N* $K_2Cr_2O_7$ direct	1.311	0.988
Against 0.2 *N* $K_2Cr_2O_7$ through ferrous ammonium sulphate solution (see discussion below)	1.301	0.979

TABLE II

Titanous sulphate solution 0.2 *N* (Fe = 0.065%)

Method of standardizing	Factor
Against standard ferric ammonium sulphate solution	1.097
Against 0.2 *N* $K_2Cr_2O_7$ direct	1.155
Against 0.2 *N* $K_2Cr_2O_7$ through ferrous ammonium sulphate solution (see discussion below)	1.097

crystals were deposited. The crystals, of $TiCl_3.6H_2O$, were quickly filtered off on a sintered glass filter funnel with the aid of gentle suction and washed with ice-cold concentrated hydrochloric acid. A 20% solution was prepared in 20% hydrochloric acid and this solution was diluted to the required strength.

Method 2. To the original commercial titanous chloride was added 10% of concentrated hydrochloric acid and the solution was carefully oxidised by the dropwise addition of concentrated nitric acid whilst warming on a water bath. To the cold solution of titanic chloride was added ammonium thiocyanate solution (10%) in small amounts, the red ferric thiocyanate formed being extracted after each addition with a mixture of equal parts of amyl alcohol and ethyl ether. When the further addition of a few drops of ammonium thiocyanate produced a yellow rather than an orange colour, a final extraction with amyl alcohol/ether mixture was made in order to remove the titanic thiocyanate formed from the excess ammonium thiocyanate. Finally, the amyl alcohol was extracted from the solution with ether, the last trace of ether being removed by warming on the water bath.

The solution was reduced to the titanous state by shaking with zinc amalgam and the acid content was increased to 40% by the addition of further hydrochloric acid. This solution was diluted to the required strength for use.

Of the two methods, the second is recommended where the iron-free solution is required for immediate use, as in the present work. Several litres of iron-free titanous chloride solution can thus be prepared in an hour or two with little loss of the original solution, whereas by the first method the yield of crystals is quite small and the operations require several days for completion. Titanous chloride solution prepared by Method 2 tends to have a shorter storage life, however, and where solutions are required to remain stable over prolonged periods Method 1 might be more suitable.

Preparation of iron-free titanous sulphate solution. Iron-free titanous sulphate cannot satisfactorily be prepared by either of the above methods. In Method 2 the sulphuric acid interferes with the extraction of the ferric thiocyanate complex. The sulphate can be quickly prepared from the iron-free chloride solution by additon of a small excess of sulphuric acid, the bulk of the hydrochloric acid being removed by boiling. The presence of some residual hydrochloric acid in the titanous sulphate solution thus prepared is unobjectionable.

Standardization of iron-free solutions. Using the iron-free titanous chloride solution, direct standardization with potassium dichromate gives good agreement with other methods, as Table III indicates.

TABLE III

Method of standardizing	Titanous chloride 0.2 *N* (prepared by Method 1)	Titanous chloride 0.2 *N* (prepared by Method 2)
Against $K_2Cr_2O_7$ direct	0.997	1.049
Against $K_2Cr_2O_7$ through ferrous ammonium sulphate solution (see below)	0.997	1.048

DISCUSSION

From the above, the following points emerge:

1. It is necessary to specify that titanous solutions must be free from iron if potassium dichromate is to be used directly as the standardizing reagent. In view of this, and of the fact that all supplies of titanous reagents examined were found to contain iron as impurity, it is better to use a method of standardization which is free from this objection. The two methods recommended are: —

(a) against a standard solution of ferric ammonium sulphate using ammonium thiocyanate as indicator.

The ferric ammonium sulphate is standardized either by reduction with stannous chloride in the usual way[7], followed by titration with permanganate, or by reduction with zinc amalgam followed by titration with potassium dichromate using *o*-phenanthroline as indicator.

(b) against potassium dichromate through ferrous ammonium sulphate solution.

The dichromate is run into excess ferrous ammonium sulphate solution which has been freshly reduced by shaking with zinc amalgam. An equivalent amount of ferric ion is formed and this is titrated with the unknown titanous solution using ammonium thiocyanate as indicator. A blank is carried out on the ferrous ammonium sulphate solution.

2. There are reasons for preferring titanous chloride to titanous sulphate as a titrant. Among these are the following:

(i) Whilst fully reduced titanous sulphate is a clear bluish solution, it is more normal to find it supplied in the partly oxidised condition when it is a muddy and opaque liquid, the meniscus of which is difficult to read accurately. Titanous chloride on the other hand does not pass through the muddy phase on partial oxidation and remains a clear violet colour throughout. There is therefore no necessity with this reagent to ensure that is it completely reduced before use.

(ii) The sulphate tends to cause more rapid fouling of the burette with consequent risk of inaccuracies due to erratic drainage. This can be minimised by the addition of a suitable wetting agent to the solution.

(iii) The chloride normally contains less iron as impurity than the sulphate.

Acknowledgement is made to the Chief Scientist, Ministry of Supply for permission to publish this paper.

SUMMARY

It is confirmed that the presence of iron as impurity in titanous chloride and sulphate solutions invalidates the use of potassium dichromate as a standard substance. Methods of overcoming this interference and of preparing iron-free titanous salt solutions are discussed and reasons are given for preferring titanous chloride to titanous sulphate for most purposes.

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RÉSUMÉ

L'auteur confirme le fait que la présence du fer (impureté) dans le chlorure ou le sulfate de titane(III) gêne la titration au moyen de dichromate de potassium (étalon). Les méthodes permettant de remédier à cet inconvénient et de préparer des solutions de sels de titane(III) exempts de fer sont décrites.

ZUSAMMENFASSUNG

Der Autor bestätigt die Tatsache, dass die Gegenwart von Eisen als Verunreinigung in Titan-III-chlorid oder -sulfat die Titration mittels Kaliumbichromat als Eichsubstanz stört. Es werden Methoden beschrieben, die es erlauben diesem Nachteil abzuhelfen und Lösungen von Titan-III-salzen herzustellen, die frei sind von Eisen.

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THE DETERMINATION OF FLUORIDE BY TITRATION WITH CALCIUM CHLORIDE

by

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Gravimetric methods for the determination of fluoride as calcium fluoride have been widely used for many years, but titrimetric methods based on this reaction have received little attention owing to the lack of suitable indicators. RINGBOM AND MERIKANTO[1] used ferric thiocyanate as indicator in the titration of calcium with sodium fluoride, but we find the colour change poor when decinormal solutions are used. KUTSCHMENT AND GENGRINOVITCH[2] titrated calcium with standard oxalate solution using cacotheline and ferrous sulphate as indicator. At the end-point the ferrous ion reduces the cacotheline to a violet colour in the presence of oxalate ions owing to a lowering of the potential of the system. Since fluoride (and phosphate) ions are known to have a similar effect we tried titrating with a fluoride solution, but no end-point could then be obtained. FREZE[3] has recommended haematoxylin as an adsorption indicator in the titration of calcium with an oxalate solution, but as in the preceding case, the method did not work when a fluoride solution was used in place of oxalate.

Although the colour reaction between calcium ions and murexide has been known for nearly a hundred years[4], it has only been exploited fairly recently for analytical purposes. SCHWARZENBACH and his colleagues[5] have used murexide as indicator in the titration of calcium with ethylenediamine tetra-acetic acid (EDTA). Calcium and magnesium have been titrated with the same reagent using Eriochrome Black T (Solochrome Black) as indicator.

We have investigated the possibility of using these indicators in the titration of fluoride with calcium. Direct titration was not satisfactory, but a method has been developed in which fluoride is precipitated as calcium fluoride and the unconsumed calcium ions back-titrated with EDTA. The method has one main disadvantage. When small amounts of calcium are determined a large back-titration is obtained. This cannot be overcome by using smaller volumes of standard calcium solution because precipitation is not then complete at fairly low levels. Nevertheless, by using Grade A burettes and careful measurement, the indicator change is so sharp that results of moderate accuracy are readily

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attainable. The method has the advantage that ions such as sulphate and phosphate (which interfere seriously when the thorium nitrate or aluminium chloride methods are used) have no effect. Although it is desirable to allow the precipitated calcium fluoride to stand overnight, the actual operating time involved is small. The method is recommended for the range 5-65 mg of fluorine; it could probably be operated above this amount (which was the highest amount we determined) but below 5 mg the results become appreciably low. Possibly smaller amounts might be determined if it were possible to reduce the volume of the solution accordingly; more dilute standard solutions could then be used.

Direct titration

When a fluoride solution was titrated with a calcium solution or *vice versa* using either indicator, the end-points were poor. Precipitation of calcium fluoride was very slow unless an excess of reagent was present. The end-points were extremely sluggish and the results were erratic.

The titration was tried in 50 per cent. ethanolic solution to accelerate precipitation. No marked improvement was noted, but when the solution was heated to about 70° C the reaction proceeded more rapidly. However, the indicator appeared to be less sensitive under these conditions and the colour change was not sufficiently sharp for practical purposes.

Back-titration with EDTA

A back-titration procedure was then tried. An excess of standard calcium chloride was added to the fluoride solution and the excess calcium was determined by titration with EDTA after various standing times. Low and erratic results were obtained, presumably due to incomplete precipitation of calcium fluoride. A 50 per cent. ethanolic medium effected some improvement, but the results were not sufficiently satisfactory. The colour change was delayed and resulted in the end-point being overshot. Although both murexide and Eriochrome Black T were satisfactory, the latter was preferred. The colour change was from red to blue and a warning of the approach of the end-point was given by a gradual change from red to purple. All further tests were carried out using Eriochrome Black T.

Conditions for precipitation

All attempts to improve the precision of the method were unsuccessful until the conditions recommended by CLARKE AND BRADSHAW[6] for the gravimetric determination were adopted in a modified form. These investigators precipitated calcium fluoride from a neutral or acetic acid medium. The mixture was then boiled for a short time and filtered after 15 min. It was not possible in the present case to use the same excess of calcium chloride as CLARKE AND BRADSHAW recommended, because the back-titration would have been excessive. It was found that when *ca.* 10 mg of fluoride ion were present in *ca.* 50 ml of solution, 20 ml of $0.1N$ calcium chloride solution were sufficient to effect quantitative precipitation, but the time of standing had then to be increased considerably. Under these conditions satisfactory results were obtained both when the excess calcium was titrated in the presence of calcium fluoride or after filtration.

The effect of pH

So far, precipitation had been effected at a pH between 6 and 7. Under these conditions it would be expected that certain ions might interfere, in particular carbonate and phosphate. Large amounts of sulphate would be expected to interfere at any pH. Recoveries were then checked at lower pH ranges. Below pH 4 somewhat low results were obtained as shown in Table I. It was concluded that precipitation would have to be effected at a pH < 4.5.

Determination of fluoride ion in the range 2-65 *mg*

Some preliminary tests on the time of standing were first carried out to establish whether or not the overnight period was necessary with the larger amounts of fluoride. These results are summarised in Table II.

Although the time of standing can be reduced considerably when moderate amounts of fluoride are present it was decided to standardise the procedure using the overnight period, rather than recommend different standing times varying with the amount of fluoride ion present.

TABLE I

EFFECT OF PH ON RECOVERY OF CALCIUM FLUORIDE

F^- added (mg)	pH	F^- found (mg)
9.94	3.0	9.60
9.94	3.5	9.64
9.94	4.0	9.80
9.94	4.5	9.92
9.94	5.0	9.90
9.94	6.0	9.92
9.94	7.0	9.92

The results obtained over the range 2-65 mg are included in Table III.

For amounts < 25 mg F^-, 20 ml $0.1N$ $CaCl_2$ added; for amounts > 25 mg 20 ml $0.2N$ $CaCl_2$ added.

TABLE II

EFFECT OF STANDING TIME ON RECOVERY

Time of standing (h)	Result
1	Incomplete recovery for all amounts
2	Complete for amounts > 20 mg
4	Complete for amounts 10-20 mg
	Low results < 10 mg, error increasing with decrease in amount of F^-
Overnight	Complete for 5 mg Rather low 2-5 mg Poor < 2 mg

TABLE III

DETERMINATION OF FLUORIDE ION IN THE RANGE 2-65 mg

F^- present mg	F^- found (mg) (mean)	No. of detns.	Largest deviation from correct amount (mg)
1.90	1.82	10	—0.17
3.80	3.77	2	—0.07
5.70	5.67	6	—0.10
7.60	7.58	2	—0.04
9.50	9.48	6	—0.08
15.20	15.23	3	+0.08
19.00	18.92	1	—0.08
28.50	28.56	2	+0.15
38.00	38.20	2	+0.30
47.50	47.52	5	+0.08
57.00	57.07	3	+0.19
66.50	66.45	3	—0.11

Interfering ions

Our object in developing this method was ultimately to examine its possible application to the determination of fluorine in organic compounds. In this case where decomposition is effected with sodium and potassium in a nickel bomb, the interfering ions likely to be present are limited consisting, after suitable treatment, of chloride, bromide, iodide, sulphate, phosphate or arsenate. Carbonate ions would be present also in every case. At a pH of 4.5 those ions which form insoluble salts with calcium in neutral solution are completely soluble; however, before titration it is necessary to add a buffer solution to raise the pH, and under these conditions the insoluble salts would precipitate. In normal circumstances it would be then impossible to determine fluoride because some of the excess calcium would be consumed by the precipitation of these insoluble salts. There was the possibility, however, that EDTA might react with these compounds, particularly when newly precipitated. This reaction was actually found to occur. When 100 mg amounts of phosphate, arsenate or sulphate were treated exactly as in the procedure for the determination of calcium (but with fluoride absent) no precipitate was observed after standing overnight at pH 4.5. When the buffer solution was added, visible precipitates appeared in the case of phosphate and arsenate, but on titrating with EDTA the whole of the original amount of calcium added was obtained. This effect may not occur, of course, with precipitates which have had a chance to age, but it is of no importance from the present standpoint.

It remained then to study whether or not this effect still persisted in the presence of calcium fluoride. When tests were carried out another curious phenomenon was noted: the end-points were poor and slowly reverted to the original colour until eventually all the original amount of calcium had been titrated. Thus in the presence of phosphate, sulphate, or arsenate there seemed to be an induced solution of calcium fluoride in EDTA. This effect was readily overcome by filtering off the calcium fluoride prior to adding the buffer.

The results of determining fluoride ion in the presence of these ions and of chloride, bromide and iodide are summarised in Table IV. In the case of the three halides no modification to the general procedure was necessary. When sulphate, phosphate or arsenate was present the precipitated calcium fluoride was removed by filtration. Carbonate does not interfere since it is removed when the solution is boiled.

The indicator change when sulphate, phosphate or arsenate was present was not as sharp as in their absence. Nevertheless it could be detected with one drop of titrant.

TABLE IV

THE DETERMINATION OF FLUORIDE ION IN THE PRESENCE OF OTHER ANIONS

Anion	Amt. added	F^- present (mg)	F^- found (mg)
Cl^-	300	9.94	9.94
Br^-	300	9.94	9.88
I^-	300	9.94	9.86
SO_4^{-2}	100	9.94	9.96
PO_4^{-3}	100	9.94	10.05
AsO_4^{-3}	100	9.94	10.01
CO_3^{-2}	100	9.94	9.97

EXPERIMENTAL

Reagents

Calcium chloride solution 0.1N

(1 ml = 1.9 mg F$^-$)

Dried "AnalaR" calcium carbonate (5.0045 g) is mixed with a small volume of water in a 600 ml beaker and 3 or 4 drops of methyl red indicator solution are added.

Hydrochloric acid (2N) is added slowly until the solution is neutral, the beaker being covered by a clock-glass to prevent losses by spirting. Carbon dioxide is boiled off and the solution cooled. After ensuring that the solution is neutral or slightly acid, it is diluted with distilled water to a volume of 1 litre. The solution may be standardised by gravimetric determination of calcium, but if sufficient care is taken during its preparation, standardisation is unnecessary. For amounts of fluoride above 20 mg a 0.2N solution is preferable.

EDTA solution 0.1N

Ethylenediamine tetra-acetic acid disodium salt (18.6 g) is dissolved in water and the solution diluted to 1 litre.

The solution is standardised by titration against standard calcium chloride solution.

Ammonia solution ca. 0.1N
Hydrochloric acid ca. 0.02N
Buffer solution

Ammonium chloride (67.5 g) is dissolved in 0.880 ammonia (570 ml) and diluted to 950 ml with distilled water. Magnesium chloride hexahydrate (0.508 g) and EDTA disodium salt (0.93 g) are dissolved in water (50 ml). The two solutions are mixed.

Indicator solution

Eriochrome Black T (0.5 g) is dissolved in ethanol (100 ml).

Procedure

(a) *Interfering anions absent*

The fluoride solution, containing between 5 and 65 mg of fluorine in a volume of 50 ml, is treated with dilute hydrochloric acid using methyl red indicator until the solution is slightly acid. For amounts < 25 mg 20 ml of 0.1N solution are used; for amounts > 25 mg 20 ml of 0.02N solution are used. Calcium chloride solution is added and the pH of the solution adjusted by careful addition of 0.1N

ammonium hydroxide solution until the red colour of the indicator is just discharged. The pH is brought to *ca.* 4.5 by dropwise addition of 0.02*N* hydrochloric acid until the indicator is a faint pink. The solution is boiled for about 15 sec and allowed to stand overnight at room temperature.

Buffer solution (1 ml) and indicator (0.3 ml) are added and the solution is titrated with 0.1*N* EDTA solution.

(b) *Interfering ions present*

The solution is treated exactly as in the preceding case. After standing overnight the precipitate is filtered on paper pulp and washed with three 10-ml portions of a 5 per cent. solution of ammonium nitrate. The precipitate and filter pad are discarded. The filtrate is titrated with 0.1*N* EDTA solution as described above.

One of us (S.J.C.) wishes to express his thanks to the Government Awards Branch (F.E.T.S.) for a grant enabling him to undertake this investigation.

SUMMARY

A new method for the determination of fluoride ions is described. Precipitation is effected with an excess of standard calcium chloride and, after standing overnight, the unconsumed calcium ions are back-titrated with ethylenediamine tetra-acetic acid (EDTA) using Eriochrome Black T as indicator. Halides, sulphate, phosphate and arsenate do not interfere under the recommended conditions. The method is applicable over the range 5-65 mg of fluoride ion.

RÉSUMÉ

Une nouvelle méthode de dosage de l'ion fluorhydrique est décrite. La précipitation est effectuée au moyen d'une solution étalon de chlorure de calcium en excès, et après une nuit le calcium en excès est déterminé par l'acide éthylènediamine tétracétique (EDTA) en présence de noir d'ériochrome T, comme indicateur. Les halogènes, sulfate, phosphate et arséniate ne gênent pas dans les conditions recommandées. La méthode permet de doser de 5 à 65 mg d'ion fluorhydrique.

ZUSAMMENFASSUNG

Es wird eine neue Methode zur Bestimmung von Fluoridionen beschrieben. Die Ausfällung wird mit einem Überschuss eingestellter Calciumchloridlösung durchgeführt und nach dem Stehen über Nacht werden die unverbrauchten Calciumionen mit Äthylendiamintetraessigsäure (EDTA) und Eriochromschwarz T als Indikator zurücktitriert. Halogenide, Sulfate, Phosphate und Arsenate stören die Reaktion bei den empfohlenen Bedingungen nicht. Die Methode ist in einem Bereich von 5-65 mg Fluorionen anwendbar.

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BEITRÄGE ZUR HALOGENIDBESTIMMUNG NACH VOLHARD

von

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Unlängst haben E. SCHULEK und E. PUNGOR[1] ein Halogenidbestimmungsverfahren veröffentlicht, in welchem das Halogenid in neutraler Lösung durch Hinzufügen von Silbernitrat in bekanntem Überschuss gefällt wird. Nach Koagulieren des Silberhalogenids mit Hilfe von Kaliumnitrat, konnte der Silberüberschuss —ohne den Niederschlag zu entfernen— in Gegenwart von *p*-Äthoxychrysoidin mit 0.01*N* Kaliumjodid-Lösung mit einer Genauigkeit von etwa ± 0.1 % bestimmt werden. Dieser Befund ist umso überraschender, da die Löslichkeit des Silberjodids 100-1000-mal kleiner, als die der Silbersalze der zu bestimmenden Halogenide ist. — Wir haben uns zum Ziel gesetzt nachzuforschen, warum der Ionenaustausch im Äquivalenzpunkt in dieser Bestimmungsmethode so günstig verlangsamt wird.

Vor allem haben wir die am häufigsten verwendete Volhard'sche Chloridbestimmung-Methode nachgeprüft, deren Fehler in der Literatur[2] auf das Chlorid berechnet, als +0.7% angegeben ist, wenn der koagulierte AgCl-Niederschlag aus dem Reaktionsgemenge entfernt, aber nicht ausgewaschen ist („aliquoter Teil Methode"). Der Mittelwert dieses Fehlers beträgt nach unseren Messungen (16 Bestimmungen), doch auf den Silberüberschuss berechnet* — 0.65 (Tabelle I). Haben wir den AgCl-Niederschlag durch Aufkochen koaguliert, den Silberüberschuss aber in Gegenwart des Niederschlages titriert, so war der Mittelwert der Fehler von 17 Bestimmungen —0.44% (Tabelle II). Wurde der Niederschlag ausfiltriert, mit heissem Wasser gewaschen und dann das mit dem Waschwasser vereinigte Filtrat titriert, so betrug der Fehler bloss —0.20% (Tabelle III).

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* Diese Ausdrucksweise wird von uns bevorzugt, da der Titrationsfehler durch die Adsorption der Silberionen verursacht wird. Um die in diesem Sinne berechneten Werte mit dem aus der Literatur bekannten Titrierfehler von +0.7% vergleichen zu können, haben wir diesen Fehler auf Silber berechnet, da der Fehler eben durch Silberionenadsorption entstanden ist. Die Umrechnung bedeutet bloss den Vorzeichenwechsel, wenn man annimt, dass die zur Chloridfällung gebrauchte Silberlösung in 100%-igen Überschuss verwendet wurde.

Literatur S. 234.

TABELLE I

Nach Fällung des Silberchlorids wurde das Reaktionsgemisch in einem Messkolben ohne Aufkochen auf 50 bzw. auf 100 ml ergänzt und die niederschlaghaltige Lösung, durch ein trockenes Papierfilter filtriert. In einem Anteil von 25.00 bzw. 50.00 ml des Filtrates wurde der Silberüberschuss titriert. Die Werte sind vergleichshalber auf 50 bzw. 100 ml bezogen angegeben. Endvolumen der austitrierten Lösung etwa 40 bzw. 80 ml.

0.1 *N* KCl-Lösung ml	0.1 *N* $AgNO_3$-Lösung ml	10%-ige HNO_3 ml	10%-ige $Fe(NO_3)_3$-Lösung ml	0.1 *N* KCNS-Lösung ml		Δ %	
				verbr.	berechn.	einzeln	im M.-Wert
5.045	19.92	20	1	14.82	14.88	—0.40	
5.045	19.92	20	1	14.80	14.88	—0.54	
5.045	19.92	20	1	14.80	14.88	—0.54	
5.045	19.92	20	1	14.78	14.88	—0.67	—0.63
5.045	19.92	20	1	14.76	14.88	—0.81	
5.045	19.92	20	1	14.76	14.88	—0.81	
20.95	50.04	4	2	28.83	29.09	—0.55	
20.95	50.04	4	2	28.95	29.09	—0.48	
20.95	50.04	4	2	28.87	29.09	—0.76	
20.95	50.04	4	2	28.87	29.09	—0.76	
20.95	50.04	4	2	28.89	29.09	—0.69	—0.67
20.95	50.04	4	2	28.85	29.09	—0.82	
20.95	50.04	4	2	28.83	29.09	—0.89	
20.95	50.04	4	2	28.89	29.09	—0.69	
20.95	50.04	4	2	28.93	29.09	—0.55	
20.95	50.04	4	2	28.93	29.09	—0.55	

Es erschien uns nun interessant zu untersuchen, welchen Einfluss die Verwendung des Kaliumnitrats, als koagulierendes Mittel in dem VOLHARD'schen Halogenidbestimmungsverfahren ausübt*. Demgemäss wurden Versuche in drei Richtungen ausgeführt.

1. Es wurden Chloridbestimmungen nach VOLHARD doch mit der Abänderung durchgeführt, dass das Silberchlorid ohne Aufkochen des Reaktionsgemisches durch Schütteln mit Kaliumnitrat koaguliert wurde. Nach den Ergebnissen der Tabelle IV war der Fehler —0.57%.

2. Wurde das gefällte Silberchlorid in Gegenwart von Kaliumnitrat aufgekocht und der Silberüberschuss in Gegenwart des koagulierten Silberchlorids mit Kaliumrhodanid titriert, so betrug der Fehler im Mittelwert —0.08% (Tabelle V).

3. Haben wir die Chloridbestimmung nach VOLHARD unter Verwendung von Kaliumnitrat nach Aufkochen als „aliquoter Teil Methode", also ohne Auswaschen des gefällten Silberchlorids ausgeführt, so war der mittlere Fehler —0.15% (Tabelle VI).

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* Ähnliche Versuche wurden von J. BITSKEI (*Z. anal. Chem.*, 118 (1940) 164), doch nicht mit den gleichen Ergebnissen, ausgeführt.

Literatur S. 234.

TABELLE II

Nach Fällung wurde das Silberchlorid durch Aufkochen der niederschlaghaltigen Lösung koaguliert und der Silberüberschuss in Gegenwart des Niederschlages titriert. Endvolumen der Lösung nach dem Titrieren etwa 40, bzw. 100 ml.

0.1N KCl-Lösung ml	0.1N $AgNO_3$-Lösung ml	10%-ige HNO_3 ml	10%-ige $Fe(NO_3)_3$-Lösung ml	0.1N KCNS-Lösung ml		△ %	
				verbr.	berechn.	einzeln	im M.-Wert
5.045	9.99	20	1	4.93	4.94	−0.20	−0.46
5.045	9.99	20	1	4.92	4.94	−0.40	
5.045	9.99	20	1	4.93	4.94	−0.20	
5.045	9.99	20	1	4.91	4.94	−0.61	
5.045	9.99	20	1	4.91	4.94	−0.61	
5.045	9.99	20	1	4.91	4.94	−0.61	
5.045	9.99	20	1	4.91	4.94	−0.61	
20.95	50.04	4	2	28.98	29.09	−0.38	−0.42
20.95	50.04	4	2	28.97	29.09	−0.41	
20.95	50.04	4	2	28.97	29.09	−0.41	
20.95	50.04	4	2	28.96	29.09	−0.45	
20.95	50.04	4	2	28.97	29.09	−0.41	
20.95	50.04	4	2	28.97	29.09	−0.41	
20.95	50.04	4	2	28.97	29.09	−0.41	
20.95	50.04	4	2	28.96	29.09	−0.45	
20.95	50.04	4	2	28.95	29.09	−0.48	
20.95	50.04	4	2	28.97	29.09	−0.41	

TABELLE III

Nach Fällung wurde das Silberchlorid ohne Kochen durch einen Papierfilter filtriert und mit heissem, mit wenig HNO_3 angesäuertem Wasser silberfrei gewaschen. In dem mit Waschwasser vereinigten Filtrat wurde der Silberüberschuss mit Kaliumrhodanid titriert. Endvolumen der titrierten Lösung etwa 100 bzw. 200 ml.

0.1N KCl-Lösung ml	0.1N $AgNO_3$-Lösung ml	10%-ige HNO_3 ml	10%-ige $Fe(NO_3)_3$-Lösung ml	0.1N KCNS-Lösung ml		△ %	
				verbr.	berechn.	einzeln	im M.-Wert
5.06	10.07	20	1	5.01	5.01	0.00	−0.13
5.06	10.07	20	1	5.00	5.01	−0.20	
5.06	10.07	20	1	5.00	5.01	−0.20	
20.95	50.04	4	2	28.98	29.09	−0.38	−0.26
20.95	50.04	4	2	28.99	29.09	−0.34	
20.95	50.04	4	2	28.98	29.09	−0.38	
20.95	50.04	4	2	29.00	29.09	−0.31	
20.95	50.04	4	2	29.00	29.09	−0.31	
20.95	50.04	4	2	29.03	29.09	−0.21	
20.95	50.04	4	2	29.04	29.09	−0.17	
20.95	50.04	4	2	29.04	29.09	−0.17	
20.95	50.04	4	2	29.03	29.09	−0.21	
20.95	50.04	4	2	29.05	29.09	−0.14	

Literatur S. 234.

TABELLE IV

Nach Fällung wurde das Silberchlorid ohne das Reaktionsgemisch aufzukochen, durch Schütteln mit Kaliumnitrat koaguliert. Der Silberüberschuss wurde in Gegenwart des Silberchlorids titriert. Endvolumen der titrierten Lösung etwa 40 bzw. 100 ml.

0.1*N* KCl-Lösung ml	0.1*N* $AgNO_3$-Lösung ml	10%-ige HNO_3 ml	KNO_3 g	10%-ige $Fe(NO_3)_3$-Lösung ml	0.10*N* KCNS-Lösung ml		△ %	
					verbr.	berechn.	einzeln	im M.-Wert
5.06	10.07	20	2	1	4.99	5.01	—0.40	—0.57
5.06	10.07	20	2	1	4.97	5.01	—0.80	
5.06	10.07	20	2	1	4.98	5.01	—0.60	
5.06	10.07	20	2	1	4.98	5.01	—0.60	
5.06	10.07	20	2	1	4.99	5.01	—0.40	
5.06	10.07	20	2	1	4.98	5.01	—0.60	
20.95	50.04	4	5	2	28.91	29.09	—0.62	—0.58
20.95	50.04	4	5	2	28.91	29.09	—0.62	
20.95	50.04	4	5	2	28.92	29.09	—0.58	
20.95	50.04	4	5	2	28.93	29.09	—0.55	
20.95	50.04	4	5	2	28.93	29.09	—0.55	
20.95	50.04	4	5	2	28.91	29.09	—0.62	
20.95	50.04	4	5	2	28.95	29.09	—0.48	
20.95	50.04	4	5	2	28.93	29.09	—0.55	
20.95	50.04	4	5	2	28.91	29.09	—0.62	

TABELLE V

Nach Fällung wurde das Silberchlorid mit Kaliumnitrat aufgekocht und 3 Minuten im Sieden gehalten. Der Silberüberschuss wurde in der abgekühlten Lösung in Gegenwart des Silberchlorids mit Kaliumrhodanid titriert.

0.1*N* KCl-Lösung ml	0.1*N* $AgNO_3$-Lösung ml	10%-ige HNO_3 ml	KNO_3 g	10%-ige $Fe(NO_3)_3$-Lösung ml	0.10*N* KCNS-Lösung ml		△ %	
					verbr.	berechn.	einzeln	im M.-Wert
5.06	10.07	20	2	1	5.01	5.01	0.00	—0.07
5.06	10.07	20	2	1	5.00	5.01	—0.20	
5.06	10.07	20	2	1	5.01	5.01	0.00	
5.06	10.07	20	2	1	5.01	5.01	0.00	
5.06	10.07	4	2	1	5.01	5.01	0.00	
5.06	10.07	4	2	1	5.00	5.01	—0.20	
20.95	50.04	4	5	2	29.06	29.09	—0.1	—0.09
20.95	50.04	4	5	2	29.07	29.09	—0.07	
20.95	50.04	4	5	2	29.06	29.09	—0.1	
20.95	50.04	4	5	2	29.06	29.09	—0.1	
20.95	50.04	4	5	2	29.06	29.09	—0.1	
20.95	50.04	4	5	2	29.07	29.09	—0.07	
20.95	50.04	4	5	2	29.06	29.09	—0.1	
20.95	50.04	4	5	2	29.07	29.09	—0.07	

Literatur S. 234.

TABELLE VI

Nach Fällung des Silberchlorids wurde das kaliumnitrathaltige Reaktionsgemisch aufgekocht, dann abgekühlt, endlich in einem Messkolben auf 100 ml ergänzt. In einem 50 ml Anteil der, durch ein trockenes Papierfilter filtrierten Lösung wurde der Silberüberschuss titriert. Die Werte sind vergleichshalber auf 100 ml bezogen angegeben. Endvolumen der austitrierten Lösung etwa 100 ml.

0.1 N KCl-Lösung ml	0.1 N $AgNO_3$-Lösung ml	10%-ige HNO_3 ml	KNO_3 g	10%-ige $Fe(NO_3)_3$-Lösung ml	0.10 N KCNS-Lösung ml		△ %	
					verbr.	berechn.	einzeln	im M.-Wert
20.95	50.04	4	5	2	29.03	29.09	—0.21	
20.95	50.04	4	5	2	29.08	29.09	—0.03	—0.15
20.95	50.04	4	5	2	29.03	29.09	—0.21	

BESPRECHUNG DER RESULTATE

Wird das gefällte Silberchlorid im Laufe der VOLHARD'schen Bestimmung durch Schütteln koaguliert, so werden an der Oberfläche desselben Silberionen in einer etwa 0.7% Chlorid entsprechenden Menge adsorbiert. Wird also das Silberchlorid aus dem, auf ein bestimmtes Volumen ergänzten Reaktionsgemenge durch Filtrieren entfernt und der Silberüberschuss in einem aliquoten Teil des Filtrates bestimmt, so erhält man auf das Chlorid bezogen um etwa +0.7% zu hohe Werte, wie dies übrigens aus der Literatur bekannt ist. Werden die Silberionen durch Auswaschen des Niederschlages aus der Adsorptionsschichte entfernt und der Silberüberschuss in dem, mit dem Waschwasser vereinigten Filtrat bestimmt, so erhält man praktisch theoretische Werte. Dies bedeutet, dass die Silberionen aus der Adsorptionsschichte verdrängbar sind.

Wird das gefällte Silberchlorid durch Aufkochen koaguliert, und somit seine spezifische Oberfläche verringert, so kann der Silberüberschuss auch in Gegenwart des Niederschlages bestimmt werden. Die Farbe des Eisen(III)rhodanids verschwindet aber langsam in dem Äquivalenzpunkt infolge langsamer Einstellung des Adsorptionsgleichgewichtes der Silberionen.

Titriert man bis zu einer, 1 Minute beständigen rötlichen Farbe, so kann der Silberüberschuss mit einem Durchschnittsfehler von etwa —0.44% bestimmt werden. Dies bedeutet, dass sich die adsorbierte Silbermenge durch Aufkochen der Lösung in nicht zu grossem Masse verringert.

Ein ganz wesentlicher Unterschied erscheint, wenn Kaliumnitrat in grösserer Konzentration in der salpetersauren Lösung vorhanden ist. In diesem Falle gelangen hydratisierte Kaliumionen in grosser Konzentration in den diffusen Teil der Adsorptionsschichte, deren innerer Teil mit Salpetersäuremolekeln von Dipolcharakter dicht belegt ist. (Vergleiche: Elektronenmikroskopische Kontrolle der Wandwirkung in den Adsorptionserscheinungen[3] (Abb. 1).) Wird das Koagulieren mit Kaliumnitrat bei Zimmertemperatur vorgenommen, so wird die Diffu-

Literatur S. 234.

sion der an der Oberfläche des Silberchlorids adsorbierten Silberionen infolge elektrostatisch abstossender Wirkung der in dem diffusen Teil der Adsorptionsschichte vorhandenen Kaliumionen stark zurückgedrängt. Der Titrierfehler beträgt in diesem Falle —0.57%. Durch diese Annahme kann erklärt werden, warum der Titrationsfehler (—0.46%) kleiner ist, wenn das Reaktionsgemenge (Silberchlorid und Silbernitrat in salpetersaurer Lösung) ohne Verwendung von Kaliumnitrat einfach aufgekocht wird. Wird das niederschlaghaltige Reaktionsgemisch in dem VOLHARD'schen Chloridbestimmungsverfahren nach Hinzufügen von Kaliumnitrat aufgekocht und dann abgekühlt mit Kaliumrhodanid titriert, so werden beinahe theoretische Werte erhalten. Dies kann damit erklärt werden, dass sich die Unordnung der in der diffusen Schichte vorhandenen Molekeln infolge Hitzebewegung vergrössert. Dadurch wird aber auch die Diffusion der an der AgCl-Oberfläche adsorbierten Silberionen begünstigt. In diesem Vorgang werden die Silberionen durch Wasser- bzw. Salpetersäuremolekeln ersetzt. Einer rückwegigen Diffusion der Silberionen steht nun die während des Abkühlens entstandene, mit Kaliumionen gesättigte, diffuse Adsorptionsschichte im Wege.

Auf Grund der experimentellen Versuche und der theoretischen Überlegungen gestaltet sich die von uns empfohlene Ausführung der VOLHARD'schen Chloridbestimmung wie folgt.

Nach der üblichen Fällung des Chlorids mit Silberüberschuss wird in dem Reaktionsgemenge 2% Kaliumnitrat gelöst, aufgekocht und 3 Minuten im Sieden gehalten. Nach Abkühlen unter 15° wird der Silberüberschuss unter Verwendung von Eisen(III)nitrat-Lösung als Indikator mit Kaliumrhodanid-Lösung titriert.

Über die theoretischen Grundlagen der SCHULEK-PUNGOR'schen Halogenidbestimmungsmethode (Zurücktitrieren des Silberüberschusses mit Jodidlösung) wird in einer zweiten Abhandlung berichtet.

ZUSAMMENFASSUNG

Die Ausführung des VOLHARD'schen Halogenidbestimmungsverfahrens wird auf Grund theoretischer Überlegungen experimentell vervollkommt. Die Grundlagen werden besprochen.

SUMMARY

VOLHARD's method of determining halogenides is improved on the basis of theoretical considerations. The latter are discussed.

RÉSUMÉ

La méthode de dosage des halogénures par le procédé de VOLHARD est examinée et perfectionnée sur des bases théoriques. Celles-ci donnent lieu à une discussion.

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A NOTE ON THE TITRATION OF LEAD CHLOROFLUORIDE PRECIPITATES USING THE VOLHARD METHOD

by

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The VOLHARD titration is often used to complete the determination of fluoride after precipitating as lead chlorofluoride. Recently, the procedure has been recommended when fluorine is determined in organic compounds containing also sulphur, arsenic or phosphorus because these last three elements form insoluble lead salts which interfere with the gravimetric finish[1]. There is no interference in the titrimetric procedure, provided that the acidity is not less than $2N$ in nitric acid.

In the discussion on the above paper, TER HAAR[2] reported that fading end-points were obtained which he ascribed to bleaching of the ferri-thiocyanate complex caused by the formation of $[FeF_6]^{-3}$ ions. This effect was not noted by BELCHER, CALDAS AND CLARK[1], although the colour obtained at the end-point faded after standing for a few minutes. However, it was always sufficiently stable to leave no doubt as to when the true end-point had been reached. The total amount of fluoride present in the method described by BELCHER, CALDAS AND CLARK rarely approached, and never exceeded, 60 mg. It is probable that TER HAAR was determining much larger quantities of fluorine, in which case it might be expected that the bleaching effect would be more pronounced. It is to be noted, however, that WOODS AND MELLON[3] state that in the colorimetric determination of amounts of iron of the order of 2 p.p.m. by the thiocyanate method, up to 30 p.p.m. of fluoride ion have no effect.

We have carried out some tests with the following objects.

1. To study the effect of varying amounts of fluoride ion on the fading.
2. To study the effect of adding suitable reagents capable of forming complexes with the fluoride ion, more stable than that formed with ferric ions.

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The effect of fluoride and fluoride-complexing agents on the ferri-thiocyanate complex

The bleaching effect of varying amounts of fluoride ion and the suppression of this effect by various reagents were studied by measuring the volume of 0.001*N* potassium thiocyanate required to restore the intensity of the bleached colour to that of a standard. The latter was prepared by adding 3 ml of 0.001*N* potassium thiocyanate to a solution containing 1 ml of saturated ferric alum in 100 ml of 2*N* nitric acid. The tests were carried out in 2*N* nitric acid at room temperature.

The results of these tests are summarised in Table I.

TABLE I

	F present mg	Masking agent ml	Sat. ferric alum. ml	*N*/1000 KCNS ml		Notes	
1.	nil	nil	1	3		Standard	No fading observed
2.	100	nil	1	10	Colour more yellow than standard		
3.	100	nil	5	3			
4.	100	10 (sat. H_3BO_3)	1	4			
5.	100	10 (40% $Al_2(SO_4)_3$)	1	5			
6.	200	nil	1	25			
7.	200	nil	5	5			

The following conclusions may be drawn from the above results:

1. Although the colour of the ferri-thiocyanate complex is bleached by fluoride ions, it is restored by adding potassium thiocyanate.
2. Aluminium ions and boric acid decrease the volume of potassium thiocyanate solution necessary to restore the colour, but they are not as effective as ferric ions.
3. In the range 0-200 mg F^-, the amount of excess potassium thiocyanate required is very small and can be virtually eliminated by adding an extra 4 ml of ferric alum indicator.

The determination of chloride in lead chlorofluoride using the Volhard titration

Various amounts of lead chlorofluoride solution were titrated by the VOLHARD procedure with the addition of nitrobenzene[4]. Varying amounts of indicator and masking agents were added. The results are summarised in Table II.

These results confirm the previous tests. There is no pronounced fading at the end-point and the bleaching effect of fluoride ions can be overcome by adding a slight excess of potassium thiocyanate. This excess is very small and can be

TABLE II

THE BLEACHING EFFECT OF VARYING AMOUNTS OF LEAD CHLOROFLUORIDE AND ITS SUPPRESSION BY COMPLEXING AGENTS

PbClF solution taken ml	F present mg	Ferric alum present ml	Complexing agent present ml	F found mg	Error mg	Notes
25.0	25.0	1	—	24.6	−0.4	Colour at end-point stable for at least 5 min
25.0	25.0	5	—	24.7	−0.3	
25.0	25.0	1	10 $Ca(NO_3)_2$	24.6	−0.4	No ppt.
25.0	25.0	1	10 $Al_2(SO_4)_3$	24.6	−0.4	
25.0	25.0	1	10 H_3BO_3	24.7	−0.3	
50.0	50.0	1	—	49.6	−0.4	
50.0	50.0	5	—	49.7	−0.3	
50.0	50.0	1	10 $Ca(NO_3)_2$	49.7	−0.3	No ppt.
50.0	50.0	1	10 $Al_2(SO_4)_3$	48.4	−1.6	
50.0	50.0	1	10 H_3BO_3	49.6	−0.4	
100.0	100.0	1	—	99.7	−0.3	
100.	100.	5	—	100.0	−0	
100.	100.	1	10 $Ca(NO_3)_2$	99.6	−0.4	No ppt.
100.	100.	1	10 $Al_2(SO_4)_3$	98.3	−1.7	
100.	100.	1	10 H_3BO_3	99.7	−0.3	
2.9765 g PbClF	216.0	1	—	216.1	+0.1	
2.9400 g PbClF	213.4	5	—	213.0	−0.4	

neglected when using 0.1 N solutions. It will be noted that the errors are always negative as would be expected.

Aluminium ions caused a greater consumption of thiocyanate and therefore gave appreciably low results. The reason for this effect is not known. In all cases the colour at the end-point was stable for at least five minutes.

When 5 ml of saturated ferric alum solution were used, the end-points appeared to be slightly more pronounced, although the effect on the thiocyanate consumption was negligible in terms of the amounts of fluoride involved. It may be noted that HOFMANN AND LUNDELL[5] recommend 5 ml of indicator in this determination.

Although amounts of fluoride ion far in excess of that used in the method of BELCHER, CALDAS AND CLARK were examined in these tests, the phenomenon noted by TER HAAR could not be reproduced. It would be surprising if larger amounts were used in his tests. Without an exact knowledge of his conditions, therefore, it is difficult to advance an explanation for his observation.

EXPERIMENTAL

Reagents

Lead chlorofluoride solution 1 ml ≡ 1.00 mg F; 13.76 g dissolved in $2N$ nitric acid

Ferric alum saturated (assay 0.065 g Fe^{+3}/ml)

References p. 238.

Aluminium sulphate solution. 40 g $Al_2(SO_4)_3.18H_2O$ per 100 ml
Boric acid solution. Saturated (about 4.5 g per 100 ml)
0.1*N silver nitrate*
0.1*N potassium thiocyanate*

METHOD

A known quantity of lead chlorofluoride dissolved in 25-100 ml 2*N* HNO_3 was transferred to a conical flask and 1 ml of nitrobenzene added for each 0.03 g Cl present. 0.1*N* $AgNO_3$ was then added until an excess of 1-4 ml was present. The solution was then shaken vigorously for about 40 sec. Measured quantities of ferric alum and complexing agent were added and the solution was titrated with 0.1*N* KCNS to a permanent pink-brown end-point. The titrations were carried out at room temperature (15° C).

SUMMARY

Since it has been reported that a fading end-point is obtained when the VOLHARD method is used for the titration of lead chlorofluoride precipitates, a wide range of fluoride concentrations has been examined using this method. The effect of adding various reagents to bind the fluoride ion has been examined. Aluminium ions and boric acid have some effect, but that of ferric ions is the most pronounced.

RÉSUMÉ

Les auteurs ont étudié l'affaiblissement du virage lors de la titration du chlorofluorure de plomb par la méthode de VOLHARD, en effectuant une série de dosages en présence de concentrations variables de fluorure. Ils ont examiné également l'influence d'autres ions réagissant avec l'ion F^-. Al^{+3} et l'acide borique réagissent, mais c'est l'effet des ions ferriques qui est le plus prononcé.

ZUSAMMENFASSUNG

Seitdem berichtet wurde, dass ein wieder verschwindender Endpunkt auftritt, wenn man zur Titration von Bleichlorfluorid-Niederschlägen die Methode nach VOLHARD benutzt, wurde ein weiter Fluorionenkonzentrationsbereich mit dieser Methode untersucht. Es wurde die Wirkung verschiedener Reagenzien untersucht, die hinzugefügt wurden um das Fluorion zu binden. Aluminiumionen und Borsäure besitzen einige Wirkung, die ausgesprochendste Wirkung aber besitzen Ferriionen.

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THE DETERMINATION OF POTASSIUM BY PRECIPITATING AS THE 12-PHOSPHOMOLYBDATE

by

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It has been known for many years that potassium forms an insoluble salt with 12-phosphomolybdic acid. Some text-books of qualitative analysis give passing mention of the reaction (*e.g.*[1]), but give no details of its use in the detection of potassium. ILLINGWORTH AND SANTOS[2], however, state that as little as 1 part of potassium in 10,000 parts of water can be detected. The only attempt to apply the reaction quantitatively, as far as we are aware, has been due to ILMENEV[3], but details are only available in the abstracts. It is stated that precipitation is effected in a volume of 10-15 ml, using 1 g of reagent for 0.01-0.1 g of potassium. The precipitate is washed with dilute nitric acid, then with a solution of sodium nitrate until free from acid and the potassium is finally determined alkalimetrically.

Because of the lack of definite information as to the optimum conditions for precipitating potassium as the 12-phosphomolybdate, we have examined the reaction in an attempt to place it on a quantitative basis. Several difficulties were encountered, but were overcome in turn, and a method has been developed which enables potassium to be determined fairly accurately and rapidly in the range 2-20 mg. It has the advantage of being as selective as the cobaltinitrite method without producing a precipitate of variable composition, but it is not as accurate as the more time-consuming classical methods.

Preparation of the reagent

12-Phosphomolybdic acid (AnalaR) was obtained commercially. It dissolved readily in water, but gave no precipitate when added to solutions containing even large amounts of potassium. Analysis of this product showed that the P_2O_5:MoO_3 ratio was 1:19.95 instead of 1:24; evidently it consisted of a mixture of other phosphomolybdic acids. Further quantities were then prepared by the method of LINZ[4], modified by HASTINGS AND INDIANI[5] and analysis of each batch showed that it corresponded to the correct ratio for the 12-phosphomolybdic acid.

Solutions of this reagent gave precipitates with potassium. Batches were later obtained from the suppliers containing a large proportion of 12-phosphomolybdic acid; this was isolated by extraction with ether according to the method of HASTINGS AND INDIANI.

Filtration of the precipitate

Precipitates of potassium 12-phosphomolybdate were prepared under various conditions, but all were very finely divided and passed through the finest filter paper or sintered-glass filter. This difficulty was finally overcome by filtering on a pad of compressed paper pulp. Later it was found that selected sintered-porcelain crucibles of porosity 4 would also retain the precipitate.

Washing the precipitate

The precipitate was washed with dilute nitric acid to free it from excess reagent. When, however, an attempt was made to wash away the nitric acid with a solution of sodium nitrate, as recommended by ILMENEV, the precipitate passed through the filter. The concentration of sodium nitrate in the wash solution was varied, but no improvement could be observed. Other electrolytes and some organic solvents were tried without success. Eventually it was found that a wash solution of potassium chloride or nitrate could be used without the precipitate passing through the filter. It was, of course, necessary to ensure that all traces of excess reagent had been removed by the nitric acid before such wash solutions could be used.

Conditions for precipitation

Since nitric acid prevented any reduction of the reagent and, in small quantities, did not affect the results, it was used throughout the present work. It was also shown experimentally that hydrochloric acid dissolved the precipitate and caused low results; it also failed to stabilise the reagent as the nitric acid had done.

Potassium 12-phosphomolybdate was precipitated in concentrations of nitric acid varying from 0 to 50% (V/V) in order to find the most favourable conditions for precipitation. The solution, containing potassium as the chloride, was evaporated to dryness and then redissolved in 1 ml of nitric acid of the appropriate concentration. The reagent was added and the mixture heated to 70-80° C.

The precipitate was washed and then treated with a known volume of a standard carbonate-free solution of sodium hydroxide, and the excess back-titrated with a standard solution of hydrochloric acid.

A gravimetric finish was also used. Since ammonium phosphomolybdate gives a precipitate of uncertain composition after drying, it was thought that the potassium compound might behave analogously, and direct weighing was not attempted. Instead a method often applied to the former precipitate was utilised, *i.e.* conversion to and weighing as lead molybdate[6]. The results were similar to those given by the alkalimetric method. In general we preferred the latter method.

The recovery of potassium decreased with increasing acid concentration. Up to a concentration of 20% (V/V) nitric acid, the losses were not marked, but above this amount they were sufficient to vitiate the determination. Accordingly 2% nitric acid was used as the acid medium for the precipitation and for the wash solution.

In later determinations precipitation was attempted from larger volumes of solution, but low results were invariably obtained.

Time of standing the precipitate

When amounts of potassium between 2 and 20 mg (the highest amount examined) were allowed to stand for periods between 3 hours and overnight, satisfactory recoveries were obtained. The recovery was incomplete, however, for amounts less than 2 mg. The effect of reducing the time of standing was next examined for the range 2-20 mg of potassium. Recovery was incomplete after 1 hour, but was satisfactory after 2 hours (Table I). A minimum period of 3 hours was selected to ensure complete precipitation.

The results of a series of determinations over the range 2-20 mg are summarised

TABLE I

EFFECT OF VARYING THE TIME OF STANDING THE PRECIPITATE

	K (mg)			
Time (h)	Present	Found	Present	Found
1	2.0	1.61, 1.72, 1.65	10.0	8.91, 8.32, 8.54
2	2.0	1.95, 1.92, 2.01	10.0	9.95, 9.84, 10.01
4	2.0	1.97, 2.00, 1.94	10.0	9.94, 10.02, 9.93
7	2.0	1.93, 2.01, 2.00	10.0	9.97, 10.02, 10.00
Overnight	2.0	1.96, 1.94 2.01	10.0	9.98, 10.01, 9.94

TABLE II

DETERMINATION OF POTASSIUM OVER THE RANGE 2-20 MG

K present (mg)	K found (mg)					
2.0	1.90,	1.93,	1.97,	1.95,	2.0,	1.95
5.0	4.98,	4.96,	5.01,	5.00,	5.01,	4.98
10.0	9.98,	9.93,	9.92,	9.90,	10.05,	10.02
15.0	14.98,	14.95,	15.00,	14.96,	15.01,	14.97
20.0	19.94,	20.05,	19.96,	20.05,	19.97,	20.09

in Table II. The results are generally slightly low, possibly because of the slight solubility of the precipitate. Similar results were obtained using the gravimetric method.

Interferences

It was known that thallium, rubidium, caesium, silver, mercurous and ammonium formed insoluble 12-phosphomolybdates (ILLINGWORTH AND SANTOS, *loc. cit.*), hence their interference was not examined. The radicals most likely to be present in the determination of potassium (*e.g.* in silicates) are calcium, sodium, lithium, magnesium, orthophosphate, sulphate, chloride and nitrate. The effect of each of these radicals and some others was examined by determining a known amount of potassium in its presence. The results are recorded in Table III.

Precipitates were formed with calcium, sodium, lithium, and magnesium at the higher concentrations, but these readily dissolved in the 2% nitric acid used to wash out the excess reagent.

It was concluded from the results in Table III that interference is negligible below the following amounts:

Cadmium	330 mg
Aluminium	280 mg
Zinc	350 mg
Iron	300 mg
Lead	70 mg
Calcium	200 mg
Magnesium	100 mg
Phosphate	210 mg

Sodium, lithium, chloride and nitrate did not seriously interference at the highest level used.

When lead was present, lead molybdate was formed. Although it was not titratable it would interfere seriously in the gravimetric procedure.

References p. 245.

EXPERIMENTAL

Method for the determination of potassium

Reagents

12-Phosphomolybdic acid

A saturated solution of 12-phosphomolybdic acid prepared according to the method of LINZ (*loc. cit.*), modified by HASTINGS AND INDIANI (*loc. cit.*).

TABLE III

INTERFERING ELEMENTS

5 mg K present in every case					
Cd present (mg)	**K found (mg)**	**Al present (mg)**	**K found (mg)**	**Zn present (mg)**	**K found (mg)**
100	5.05	100	4.95	100	5.05
200	4.90	200	5.05	200	4.95
300	4.95	300	5.20	300	5.10
400	6.10	290	5.20	400	5.90
350	5.25	280	5.05	350	4.95
340	5.20			360	5.25
330	4.95				
Fe present (mg)	**K found (mg)**	**Pb present (mg)**	**K found (mg)**	**Na present (mg)**	**K found (mg)**
100	4.90	100	6.35	100	4.98
200	5.05	50	4.95	300	5.01
300	5.05	70	5.05	500	5.03
400	5.75	80	5.20	1000	4.97
350	5.55			2000	4.99
310	5.25				
Li present (mg)	**K found (mg)**	**Ca present (mg)**	**K found (mg)**	**Mg present (mg)**	**K found (mg)**
100	4.97	100	4.98	50	5.01
150	4.98	200	5.01	100	5.03
200	5.10	300	5.25	150	4.72
		260	5.04	105	4.91
PO_4^{-3} present (mg)	**K found (mg)**	**Cl^- present (mg)**	**K found (mg)**	**NO_3^- present (mg)**	**K found (mg)**
100	5.01	100	4.97	100	5.00
200	5.03	200	5.01	200	4.96
300	5.51	300	5.03	300	5.02
250	5.42	500	4.98	500	4.97
210	4.98				
220	5.10				
230	5.19				

References p. 245.

Nitric acid wash solution

A 2% solution (V/V) of nitric acid.

Potassium chloride wash solution

A saturated solution of potassium chloride in water. Potassium nitrate may also be used.

Preparation of the filter pad

Place a Witt filter-plate in a 3 in. funnel and cover with a layer of paper pulp. Compress the layer tightly using a glass rod with a disc at the end about 0.5 in. in diameter. Place a disc of Whatman No. 42 filter paper on top of the pulp, cover this with a further layer of pulp and again compress tightly. Place a second disc of filter paper on this second layer, cover it with a third layer of pulp and compress again. The filter bed obtained should not be less than 0.25 in. in depth.

A sintered porcelain crucible may be used in place of the above filter, but is less convenient if the determination is to be completed alkalimetrically, for the precipitate dissolves but slowly in the standard alkali. It may be used, however, when very small amounts of precipitate are involved.

Procedure

Evaporate the solution containing potassium to dryness in a 100 ml beaker and dissolve the residue in 1 ml of water. Add 5 ml of the reagent and 2 drops of concentrated nitric acid, and heat to 70-80° C. The colour of the precipitate and reagent should turn from yellow to orange, which serves as a useful indication of the temperature. Maintain at this temperature for 1-2 minutes and remove from the source of heat. Allow the precipitate to stand for 2 hours or overnight, filter under suction and wash with 2-ml portions of 2% nitric acid, allowing each portion to drain before adding another until the precipitate is free from excess reagent. Wash with five 2-ml portions of potassium chloride solution, draining well before each new addition. Transfer the pad and precipitate to a 250 ml "CO_2" flask fitted with a two-holed rubber bung. Cover the pad with about 50 ml of water and disintegrate it with a glass rod. Add phenolphthalein indicator, insert a soda-lime guard tube into one of the holes of the bung, fit the bung into the mouth of the flask and run in an excess of standard carbonate-free sodium hydroxide with the tip of the burette passing through the second hole of the bung. Seal the second hole with a piece of glass rod and swirl the contents of the flask until the precipitate has dissolved completely. Back-titrate with standard hydrochloric acid. The following reaction was assumed to take place

$$K_3PO_4.12\,MoO_3 + 23\,NaOH \rightarrow 11\,Na_2MoO_4 + K_2MoO_4 + NaKHPO_4 + 11\,H_2O$$

$$23\,NaOH \equiv K_3\,PO_4.12\,\,MoO_3$$

$$\therefore 1\text{ ml } N/10\text{ NaOH} = 0.510\text{ mg } K^+$$

Gravimetric determination

Dissolve the precipitate off the filter with 15 ml of 1:2 ammonia solution and dilute to 100 ml with hot water. Add formic acid dropwise until the solution is neutral to methyl red, and then add 4 ml in excess. Add 10 g of ammonium chloride and a little paper pulp and heat to boiling. Precipitate lead molybdate by adding an excess of lead acetate solution, digest for 5 minutes and filter on a paper-pulp pad[7]. Wash with hot 5 per cent. (w/v) ammonium nitrate solution. Ignite at a temperature not exceeding 700° C.

Wt. of ppt. X 0.02662 = wt. of K.

One of us (J.W.R.) wishes to express his gratitude to the Government Awards Branch, F.E.T.S., for a grant enabling him to undertake this investigation.

SUMMARY

A method for the determination of potassium based on precipitation as the 12-phosphomolybdate has been developed. The precipitate may be titrated alkalimetrically or converted to lead molybdate and determined gravimetrically. The main interferences are thallium, silver, mercurous, caesium and rubidium.

The method is as selective as the cobaltinitrite method without producing a precipitate of variable composition, but is not as accurate as the more time-consuming classical methods.

RÉSUMÉ

Une méthode de dosage du potassium, précipité sous forme de 12-phosphomolybdate, est proposée. Le précipité peut être titré par alcalimétrie, ou transformé en molybdate de plomb et dosé par gravimétrie. Les principaux éléments gênants sont: thallium, argent, mercure, césium et rubidium. La méthode est aussi sélective que celle au cobaltinitrite, sans donner un précipité de composition variable, mais elle est moins précise que les méthodes classiques moins rapides.

ZUSAMMENFASSUNG

Es wurde eine Methode für die Bestimmung von Kalium entwickelt, die sich auf seine Ausfällung als 12-Phosphomolybdat gründet. Der Niederschlag kann alkalimetrisch titriert werden oder in Bleimolybdat übergeführt und gravimetrisch bestimmt werden. Hauptsächlich störend wirken Thallium, Silber, Quecksilber, Caesium und Rubidium.

Die Methode ist so spezifisch wie die Cobaltinitritmethode, ohne jedoch einen Niederschlag von wechselnder Zusammensetzung zu geben, aber nicht so genau wie die mehr Zeit erfordernden klassischen Methoden.

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GRAVIMETRIC DETERMINATION OF GOLD WITH SODIUM SALT OF N-(N-BROMO-C-TETRADECYL BETAINYL)-C-TETRADECYL-BETAINE

by

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In most gravimetric methods, gold is reduced to the metallic state and weighed in this form. A wide variety of both inorganic and organic reducing agents have been recommended[4, 5, 8, 13, 19]. The metal usually separates from dilute solutions in such a finely divided state that it is not completely retained by the finest filter paper[15].

Beamish, Russell and Seath[1] report the quantitative separation of gold in cold solution and the metallic gold is formed in large enough particles so that it may be easily filtered without loss. The use of these reagents avoids errors due to finely divided particles passing through the filter, but it is difficult to transfer all traces of the solid to the filter because of the tendency of metallic gold to adhere to the sides of the beaker.

A number of organic reagents precipitate gold quantitatively in the form of complex compounds which can be easily transferred and filtered without loss. Unfortunately most of these complexes do not have a constant composition or at least cannot be washed free of impurities. This necessitates ignition and weighing as the metal, which sacrifices the advantage of a favorable weight factor. **Maynard**[10] separated gold from platinum and palladium by forming the slightly soluble gold complex of tetramethylammonium chloride. Glucose was then used as a reducing agent because ignition of the compound did not yield the metal in a pure form. **Thompson, Beamish and Scott**[17] report the quantitative separation of gold as the yellow dimethylglyoxime complex from solutions containing metals of the platinum group. The organic residue was burned off and the metal weighed. **Spacu and Kuras**[7, 16] determined gold by precipitating the amorphous yellow mercaptobenzene-thiazole complex, filtering, igniting and weighing the metal. **Kuras**[6] found that gold, copper, silver, bismuth, lead and mercury are precipitated quantitatively by 2-mercaptobenzimidazole. The compounds are

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obtained in filterable form and the organic residue may be removed by ignition.

BERG AND ROEBLING[2] report that the cations of the hydrogen sulfide group form slightly soluble complexes with thioglycolic acid and thionalide. It is stated that the metals may be determined by weighing the thionalide complexes after drying at 105° C. These authors have applied this method to the determination of copper, silver, mercury and bismuth. UMEMURA[18] used thionalide for the determination of gold. The complex was heated at a temperature below 230° C.

Studies in this laboratory on the reactivity of certain organic compounds with inorganic ions, revealed that both N-bromo-C-tetradecyl betainyl chloride-triamylamine, $C_{33}H_{111}O_3N_3ClBr$, and the sodium salt of N-(N-bromo-C-tetradecyl betainyl)-C-tetradecyl betaine, $C_{38}H_{78}N_2O_4.NaBr$, form bright yellow precipitates when added to an auric chloride solution. The latter compound, being an intermediate in the preparation of the former and simpler in structure, was chosen for a detailed investigation in the hope of developing a gravimetric method for gold that would be free of the disadvantages encountered in the reduction methods, and in which the gold could be weighed as a constituent in a high molecular weight compound. Preliminary investigation showed that the yellow precipitate could be dried to a constant weight at 85° C without decomposition. The reagent reacts with only a few other ions.

Apparently no reactions between a C-tetradecyl betaine derivative and gold have been reported in the literature. Betaine itself may be identified by preparing its gold complex which melts at 209° C[14]; the suggested formula being $C_5H_{12}NO_2 \cdot AuCl_4 \cdot 1\frac{1}{2}H_2O$. WHITMORE AND SCHNEIDER[20] employed betaine to identify gold microscopically.

APPARATUS AND SOLUTIONS

Apparatus

Selas filtering crucibles, # 10, porosity 2-5 microns, were used for filtering samples which were to be ignited.

Pyrex F, fritted glass filtering crucibles may be used if no ignition is made.

Standard Gold Solutions

a. Auric chloride

Dissolve 1.0000 g of pure gold in a mixture of 13 ml of concentrated HCl and 1.5 ml of concentrated HNO_3. After the reaction is complete, wash down the sides of the beaker with water and evaporate to 5 ml. Add 2 or 3 ml of concentrated HCl and dilute to a litre. It is not necessary to remove all of the nitrate. The solution may be analyzed by electrodeposition of gold on a platinum dish from cyanide solution[3, 12] and should contain 1.00 mg of gold per ml.

b. Auric bromide

Dissolve 0.2500 g of pure metallic gold in a mixture of 50 ml of 40 or 48%

HBr and 20 ml of 3% H_2O_2. Evaporate the solution to 30 ml to remove bromine, cool and dilute to 250 ml. This solution contains 1.00 mg of gold per ml, is approximately 1*N* in HBr, and is free of chloride.

Reagent solution

Dissolve 0.500 g of the reagent in warm water (85° C), cool and dilute to 50.0 ml. This solution becomes turbid on standing a day or two and a fresh solution must be prepared.

Solutions of diverse ions

Solutions containing 1 mg per ml of various ions[21] were prepared to check the reactivity of the reagent and to study the separation of gold from some of the interfering ions.

Stannous chloride solution

Heat 100 g of $SnCl_2 \cdot 2H_2O$ in 100 ml of concentrated HCl until a clear solution is obtained, cool and dilute to 500 ml with water.

Reagents and chemicals

Hydrobromic acid, Baker's Analyzed 48% or Merck Reagent 40%.
*Iso*propyl ether, Eastman's No. 1193.

PROPERTIES OF THE REAGENT

The sodium salt of N-(N-bromo-C-tetradecyl betainyl)-C-tetradecyl betaine, $C_{38}H_{78}N_2O_4 \cdot NaBr$, obtained from the Jackson Laboratory of the E. I. du Pont de Nemours Company[9] is a white, crystalline solid melting at 186-90° C. Recrystallization from water does not change the melting point. Theoretical composition: C, 62.53; H, 10.77; N, 3.84; Br, 10.95; Na, 3.15. Analysis: C, 61.77; H, 10.48; N, 3.60; Br, 11.43, 11.32; Na, 3.07, 2.90.

The compound dissolves readily in ethanol, warm water and 1*N* sodium hydroxide, but is only slightly soluble in ether, acetone and benzene. It dissolves in 1*N* hydrochloric acid, but within six hours the solution sets to a gel. The solubility in water at room temperature is about 0.8 g/100 ml. The compound forms a fairly stable supersaturated aqueous solution which yields a precipitate on standing. The 1% reagent solution used in these studies is usually stable from 24 to 36 hours. In some cases, especially when there is a marked drop in temperature, a solid separated in 12 hours from solutions as dilute as 0.25%. A solution which has become turbid may be cleared up by warming, but such solutions often give very finely divided precipitates of the gold complex. Hence, only freshly prepared reagent solutions should be used.

PRECIPITATION OF THE GOLD COMPLEX FROM HYDROCHLORIC ACID SOLUTION

Experiments showed that gold can be precipitated quantitatively from auric chloride solutions 1*N* in HCl and containing from 2 to 20 mg of gold per 25 ml of solution. The finely divided, bright yellow precipitate turns an orange color on drying to constant weight at 85° C. Analysis: C, 43.06, 43.10; H, 7.77, 7.18; N, 2.45, 2.50; halide (as Cl), 21.16, 21.18; Au, 22.14 ± 0.06 (average of eight determinations). The values for chloride were obtained by a Mohr titration in ethanol solution. No reasonable formula for the complex can be deduced from the above analysis. The precipitate melts at 114-15° C and decomposes at 190-200° C with evolution of gas, leaving a residue of carbon and metallic gold. The complex is soluble in acetone, ethanol, *iso*propanol, ethyl and *iso*propyl ether, ethyl acetate, acetic acid and hot water; insoluble in cold water, dilute hydrochloric acid, ligroin and carbon tetrachloride. The solubility of a dried sample in cold water and in 0.1*N* HCl is less than 1 mg per litre, but decomposition to metallic gold occurs after shaking several days with water.

Several serious disadvantages were encountered in determining gold by precipitation from hydrochloric acid solutions. The precipitate first separates in coarse, flocculent particles which decrease in size as more reagent is added. With enough reagent to insure complete precipitation, the particles become so finely divided that the precipitate must be allowed to settle in a cool place for twelve hours before filtering. Filtration is extremely slow and washing is difficult, the two processes requiring about 90 minutes for a precipitate containing 20 mg of gold. The pores of the filter become clogged if more than very gentle suction is applied. The precipitate is peptized by water and must therefore be washed with 0.1*N* HCl. More than 15% excess reagent causes peptization and gives low results. Increasing the acid concentration, adding electrolytes, heating, or cooling the precipitate does not improve the procedure.

PRECIPITATION OF THE GOLD COMPLEX FROM HYDROBROMIC ACID SOLUTION

A dark red precipitate is obtained on adding the reagent to an auric chloride solution which has been acidified with hydrobromic acid. This precipitate is not peptized by a moderate excess of the reagent, settles rapidly, may be filtered without delay and washed with distilled water without loss.

Unless otherwise stated, the procedure used in this investigation was as follows: Transfer an accurately measured volume of the standard gold solution to a 100-ml beaker, add hydrobromic acid to adjust the acidity, and dilute to 20-25 ml. Add 1% reagent solution dropwise from a burette, with stirring. When the flocculent red precipitate suddenly becomes finely divided and settles less rapidly, add 5 to 10% more of the reagent. Allow the precipitate to settle a few minutes and filter with gentle suction through a Selas #10 or a Pyrex F filtering crucible. Wash with distilled water until excess reagent is removed and dry to constant weight at 85° C. If a Selas crucible is used, the precipitate after weighing may be ignited to metallic gold. To do this, place the Selas in a porcelain crucible and heat over a low flame until no more white smoke is given off and a black deposit of carbon has formed. Then ignite at the full heat of a Meker burner for fifteen minutes, cool and weigh. When the weight of gold as well as that of the precipitate is determined, it is necessary to weigh the empty crucible both after drying at 85° C and after ignition.

Effect of hydrobromic acid concentration

The results obtained by precipitating gold from solutions of various acid concentrations are shown in Table I. Precipitation is complete in solutions which are 1 to 3 normal in HBr.

TABLE I

EFFECT OF HBr CONCENTRATION ON PRECIPITATION

5.0 mg Au and 1.9 ml of 1% reagent added

Conc. of HBr N	Wt. Ppt. mg	Wt. Au on ignition mg
1	27.8	5.0
1	27.0	4.8
2	27.9	5.0
2	27.8	5.0
3	27.6	5.0
3	27.9	5.1

McBRYDE AND YOE[11] have shown that the color of the bromaurate ion may be used to detect gold in concentrations as low as 0.5 ppm. Thus if a filtrate placed in a 50-ml Nessler cylinder cannot be distinguished from distilled water, it contains less than 0.025 mg of gold. Filtrates from the above precipitations were colorless except in the case of the $3N$ acid solutions; these latter filtrates contained about 0.05 mg of the metal. An acid concentration of $2N$ was chosen for all further precipitations.

Effect of reagent concentration

As the reagent is added dropwise to an auric bromide solution, the precipitate separates in large agglomerates. When 1.8 ml of 1% reagent solution has been added for each 5 mg of gold, the precipitate suddenly becomes finely divided, appears crystalline and settles less rapidly. Peptization does not occur at this point as in the case of solutions acidified with hydrochloric acid, but the change in character of the precipitate is quite distinct.

Varying volumes of 1% reagent were added to 20 ml of solutions containing 5.0 mg of Au and 6 ml of 7*N* HBr. The data are recorded in Table II.

TABLE II

EFFECT OF REAGENT CONCENTRATION ON PRECIPITATION

5.0 mg Au added 2*N* HBr

Reagent 1% soln. ml	Wt. Ppt. mg	Wt. Au on ignition mg
1.60	26.0	4.6
1.80	26.5	4.7
1.90	27.8	5.0
1.90	27.6	5.0
2.10	27.6	5.0
2.10	27.9	5.0
2.30	27.9	5.0
2.30	27.9	4.9
3.30	27.0	4.1

A ratio of one mole of reagent to one gram-atom of gold requires 0.37 ml of 1% reagent solution for each milligram of gold. This corresponds to 1.85 ml of the reagent for 5 mg of the metal. The results in Table II show that precipitation is not complete with 1.80 ml, but is complete when 1.90 ml of the reagent are added. As much as 25% excess reagent (2.3 ml) may be added without affecting the precipitation quantitatively, but filtration is slower. The precipitate is appreciably soluble in 75% excess (3.3 ml) of reagent. Best results are obtained by adding from 5 to 10% more of the reagent after the flocculent precipitate suddenly becomes finely divided.

Other factors affecting precipitation

a. Temperature

Precipitations are satisfactory at temperatures below 26° C, but are not complete at 30° C.

b. Concentration of gold

The volume of the solution should be as small as is convenient (10 to 25 ml). With a gold concentration of at least 0.2 mg per ml, it is easier to observe when an equivalent amount of the reagent has been added. Quantitative results, however, have been obtained with samples containing only 0.5 mg of gold in 50 ml. If the gold concentration is less than 1 mg per 20 ml the precipitate should be allowed to settle for an hour before filtering.

Filtering and washing the precipitate

Filtration through a Selas #10 or a Pyrex F filtering crucible with gentle suction is rapid and even the finest particles are retained by the filter. Four or five washings with distilled water are sufficient to remove excess reagent, though fifteen or twenty washings do not dissolve a detectable amount of precipitate. A small portion of the wash water (2 ml) may be tested for the presence of reagent by adding 4 or 5 drops of 1*N* $SnCl_2$ solution. A reagent concentration of 5 micrograms per millilitre is enough to cause a faint turbidity; higher concentrations yield a white precipitate.

Drying the precipitate

The dark red complex may be dried to constant weight at 85° C in an hour or two. Gradual decomposition occurs at 105° C. Two samples dried to constant weights of 27.6 and 27.9 mg in two hours did not change weight when heated at 85° C for 24 hours. These samples, however, lost 2.3 and 2.4 mg respectively when the temperature was raised to 105° C for 10 hours. This loss in weight was accompanied by a change in color from dark red to brown.

DETERMINATION OF GOLD IN AURIC BROMIDE SOLUTIONS

Solutions of known gold content were prepared with both the standard auric chloride and the standard auric bromide solution. The concentration of HBr in each solution was 2*N* and the total volume 20 to 25 ml. A 5% excess of 1% reagent solution was added to each. Results are recorded in Table III. The

TABLE III

DETERMINATION OF GOLD IN AURIC BROMIDE SOLUTIONS

2*N* HBr, 5% excess reagent			
Au Present mg	Wt. Ppt. mg	Au on ignition mg	Au in compound %
10.0	55.4	9.9	17.87
10.0	55.6	10.0	17.99
5.0	27.8	5.0	17.99
5.0	27.6	5.0	18.12
5.0	27.9	5.0	17.92
5.0*	27.2	4.9	18.02
5.0*	27.5	5.0	18.12
5.0*	27.1	4.9	18.08
1.0	5.1	0.8	—
1.0	5.4	0.8	—
1.0	5.6	1.0	—
			Av. 18.01 ± 0.07

* Sample free of chloride

chloride evidently does not take part in the complex formation since the solutions which were free of chloride gave the same results as the others. Furthermore, analysis of the precipitate showed no chloride.

Composition and properties of the gold complex

As already mentioned, complete precipitation is obtained with one mole of reagent for each gram-atom of gold. It seems probable that the bromide on the quaternary nitrogen of the reagent is replaced by a bromaurate ion, the complex being represented by $C_{38}H_{79}N_2O_4AuBr_4$. Calculated percentages: C, 39.90; H, 6.91; Br, 28.00; Au, 17.24. Analysis: C, 37.03, 36.94; H, 6.13, 6.32; Br, 25.57, 25.83; Au, 18.01. From these values, the calculated atom ratios of C:H:Br:Au are 38.0:76.8:3.96:1.12. These ratios indicate that one mole of reagent is associated with four atoms of bromine and approximately one atom of gold. The formula may not exactly represent the composition of the complex, but no other reasonable one conforms as well to the analyses obtained. The gold content of the precipitate is constant at 18.01% ± 0.07% and this value may be used as an empirical conversion factor.

The compound softens at 120° C and melts to a viscous liquid at 130-135° C. It is soluble in acetone, ethanol, *iso*propanol, ethyl and *iso*propyl ether, ethyl acetate, acetic acid and hot water; very slightly soluble in cold water, dilute mineral acids, ligroin and carbon tetrachloride.

REACTIONS WITH OTHER IONS

Spot-plate tests

The reagent was tested on a spot-plate for reaction with about 80 different ions as described in a previous paper[21]. In some cases, the reagent solution was also added to 5 ml of the solution of the diverse ion in a small test tube. In 1*N* HCl solution, the reagent gives white precipitates with Bi^{+3}, Sn^{+2}, Hg^{+2}, OsO_4^{-2} and $PtCl_6^{-2}$; yellow precipitates with $AuCl_4^{-1}$ and Ir^{+4}. In 2*N* HBr solution, a precipitate is obtained with Pb^{+2} and Pd^{+2} as well as with those ions which are precipitated from hydrochloric acid solution. The colors of these precipitates are: Hg^{+2} and Sn^{+2}, white; Bi^{+3}, pale yellow; $PtBr_6^{-2}$ and OsO_4^{-2}, yellow; Ir^{+4}, orange-red; Pb^{+2} and $AuBr_4^{-1}$, dark red. The reaction with platinum is being investigated at present. As would be expected Ag^{+1}, Hg^{+1} and Tl^{+1} precipitate when a solution is acidified with HCl or HBr; tungstic acid also precipitates from acid solution. Lead bromide is soluble in 2*N* HBr, but lead chloride is precipitated from 1*N* HCl solution. Bismuth and tungsten do not usually occur with gold. Tin and mercury can be present only in the higher valence states in auric halide solutions, and the metals which form insoluble halides can be removed before gold is precipitated. Interfering ions are: Hg^{+2}, $PtBr_6^{-2}$,

Ir^{+4}, Pd^{+2}, and OsO_4^{-2}. Gold may be separated from all of these by extracting it with *iso*propyl ether from a solution 2.3*N* in HBr[11].

Precipitations in presence of certain ions

Gold was determined quantitatively in the presence of lead, silver, ruthenium, and rhodium. The results are summarized in Table IV.

TABLE IV

DETERMINATION OF GOLD IN PRESENCE OF CERTAIN IONS

5.0 mg of Au added

Conditions	Wt. Ppt. mg	Au on ign. mg
AgCl, $PbCl_2$, sat. soln. diluted tenfold, 1*N* HCl	22.4	5.0
	22.5	5.0
	22.5	5.0
AgBr, sat. soln., 2*N* HBr	27.0	5.0
	27.5	5.0
Ru and Rh, 10 mg each, 2*N* HBr	27.0	4.9
	27.5	5.0

Lead bromide is appreciably soluble in HBr and such solutions give a white precipitate on addition of the reagent. Attempts to avoid interference by removing lead ions as the chloride or bromide were not successful. If this element is present, it must be removed as the sulfate, or precipitation of the gold complex must be made from hydrochloric acid solution. In the latter case lead and silver are removed as chlorides. The resulting saturated solution of lead chloride and silver chloride is diluted tenfold, the acidity adjusted to 1*N* with HCl and the gold determined in the same way as from HBr solution except that the precipitate must stand for twelve hours before filtering. This method is not recommended if more than 5 mg of gold are present, as filtering and washing the precipitate is too tedious with larger amounts.

SEPARATION OF GOLD FROM INTERFERING IONS

McBRYDE AND YOE[11] have reported the quantitative separation of gold from interfering ions by extracting the gold into *iso*propyl ether from hydrobromic acid solution. Procedure: Adjust the volume of the solution containing gold and the other ions to 10-12 ml, add 5 ml of concentrated HBr and extract the solution three times with 10 ml portions of *iso*propyl ether. The gold passes quantitatively into the ether phase. Combine the ether solutions and extract with three 20 ml portions of distilled water. The water removes the gold completely from the ether.

Evaporate the aqueous extract to dryness on a steam bath, and take up the residue with 10 ml of HBr and 1 ml of 3% H_2O_2. Remove the bromine by evaporating to 6 ml, cool, and dilute to 20 ml to make a solution approximately 2*N* in HBr. Determine gold by the method given for auric bromide solutions.

This procedure was applied to solutions containing gold alone and gold in the presence of interfering ions. The results are shown in Table V. The solutions containing only gold were evaporated after extraction and the small residue from each taken up in hydrobromic acid and hydrogen peroxide. Colorimetric tests showed that less than ten micrograms of gold remained in the hydrobromic acid solution after three ether extractions.

A solution of each of the interfering ions was run through the extraction process. The aqueous extracts were evaporated to dryness in each case. There was no residue except in the aqueous extract from the solution containing platinum. The ignited residues from the solutions that contained both gold and platinum were grey, instead of the usual yellow color of ignited gold. The data (Table V) show, however, that the amount of platinum extracted along with the gold does not appreciably affect the results.

TABLE V

DETERMINATION OF GOLD AFTER SEPARATION FROM INTERFERING IONS

5.0 mg Au added

Other Metals Present	Wt. Ppt. mg	Au found (calculated) mg	Au on ignition mg
none	27.0 27.5	4.9 5.0	4.9 5.0
Os, 10 mg	27.1	4.9	4.8
Pt, 10 mg	26.8	4.8	5.0
Pt, Pd, Ir, 10 mg ea.	26.9	4.8	4.8
Pd, Ir, 10 mg ea.; Hg, 150 mg	27.7	5.0	5.0
Pt, Pd, Ir, Os, 10 mg ea.; Hg 150 mg	27.0	4.9	5.0

DETERMINATION OF GOLD IN ORE CONCENTRATES

Roast one assay ton (29.17 g) of the sample in a large porcelain evaporating dish at the full heat of a Meker burner as long as fumes are given off. The sample should be stirred thoroughly from time to time with a porcelain spatula during the several hours of heating. Allow the sample to cool and transfer it to a 400-ml beaker after breaking up any clinkers. Add 200 ml of aqua regia (3 HCl:1 HNO_3) and digest the sample, with periodic stirring, at the boiling temperature for at least an hour. Dilute with 100 ml of water and filter with the aid of suction through a 7-cm Buchner funnel, using Whatman No. 1 paper. After the precipitate has been washed thoroughly, it is discarded.

Evaporate the filtrate and washings almost to dryness on a steam bath; add 50 ml of concentrated HCl and again evaporate almost to dryness. Take up the residue in 200 ml of water containing 10 ml of concentrated HCl. Filter off any silica which remains, catching the filtrate in a 600-ml beaker. Add 8 ml of a 0.1% solution of tellurous acid. Then run in stannous chloride solution, a little at a time with constant stirring, until a finely-divided, dark brown precipitate of tellurium forms. Add 5 to 10 ml of the stannous chloride in excess and warm the solution just below the boiling point for about ten minutes to coagulate the precipitate. Filter through a fritted glass filtering crucible, transferring and washing the precipitate with 1*N* HCl. A few drops of tellurous acid solution should be added to the filtrate to show that there is an excess of stannous chloride present.

Dissolve the black residue from the filter with three small portions of HBr containing either a little HNO_3 or H_2O_2. Wash the filter two or three times with water. Evaporate the extracts and washings nearly to dryness. Take up in 1:1 HBr and again evaporate to about 5 ml, at which point the solution will be approximately 9*N* in HBr.

If interfering members of the platinum group metals are suspected, the gold should be separated by extraction with *iso*propyl ether and determined according to directions in the preceding section. If no interfering ions are present, cool, dilute to 15-20 ml and add 1% reagent solution dropwise until the precipitate becomes finely divided and settles slowly. Then add 5% excess reagent. If only a small amount of gold (1 mg or less) is present, set the sample aside for an hour in a cool place. Filter through a Selas #10 or a Pyrex F filtering crucible, wash with 0.1*N* HBr and then with water. Dry the precipitate to constant weight at 85° C. Multiply the weight of the precipitate by 0.1801 to obtain the weight of gold. The milligrams of gold correspond to ounces per ton, if an assay ton of the sample was used.

Application of procedure

Three ore concentrates, supplied through the courtesy of the Anaconda Copper Mining Company, were analysed for gold. The results are shown in Table VI.

The results obtained are a little lower than the corresponding assay values, except in one determination. The values given by the gravimetric and colorimetric methods are in good agreement except for the first gold concentrate. The slightly low results may be due to the difficulty of extracting gold completely

TABLE VI

THE DETERMINATION OF GOLD IN ORE CONCENTRATES

Material	Gold in oz/ton		
	Assay Value[1]	Gravimetric Determination	Colorimetric Determination[2]
Au concentrate	0.985	0.79 0.85	0.99 0.95
Au concentrate	0.820	0.72 0.83	0.73 0.89
Cu concentrate	1.260	1.17 1.19	1.14 1.16

[1] Supplied by the Anaconda Copper Mining Co.

[2] Colorimetric determinations by another analyst[11] using a method involving the measurement of the color intensity of the bromaurate ion. Colorimetric determination made on each sample before the gold was precipitated.

from an ore by a wet method, or the assay values may be a little high due to traces of the platinum group metals. This procedure can be recommended for the determination of small amounts of gold in ores and concentrates if facilities for a fire assay are not available.

SUMMARY

The sodium salt of N-(N-bromo-C-tetradecyl betainyl)-C-tetradecyl betaine is presented as a gravimetric reagent for the determination of gold. Two complexes have been isolated; one, precipitated from hydrochloric acid solution, containing 22.14% gold; the other, from hydrobromic acid solution, containing 18.01% gold. Both complexes may be dried to constant weight at 85° C, thus giving the advantage of a favorable weight factor. Determinations from hydrobromic acid solutions are more rapid and offer several other advantages. Optimum conditions have been established. The number of interfering ions is small and a method for the separation of gold from these ions was developed. A procedure for the determination of gold in ore concentrates was applied to several samples with satisfactory results.

RÉSUMÉ

Le sel de sodium de la N-(N-bromo-C-tétradécyl bétainyl)-C-tétradécyl bétaîne peut être utilisé comme réactif pour un dosage gravimétrique de l'or. Deux complexes ont été isolés: l'un précipite en solution chlorhydrique, il renferme 22.14 % d'or; l'autre précipite en solution bromhydrique, il renferme 18.01 % d'or. Ces deux complexes peuvent être séchés à la température de 85° C. Les dosages effectués avec l'acide bromhydrique sont plus rapides et plus avantageux. Les conditions optima ont été établies. On propose une méthode pour séparer l'or des ions gênants, ces derniers sont d'ailleurs peu nombreux. On décrit également un dosage d'or dans les minerais enrichis.

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ZUSAMMENFASSUNG

Das Natriumsalz von N-(N-bromo-C-tetradecylbetainyl)-C-tetradecylbetain kann als Reagenz für die gravimetrische Bestimmung von Gold verwendet werden. Es wurden zwei Komplexe isoliert. Der eine Niederschlag aus chlorwasserstoffhaltiger Lösung; er enthält 22.14% Gold; der andere Niederschlag aus bromwasserstoffhaltiger Lösung; er enthält 18.01% Gold. Diese beiden Komplexe können bei einer Temperatur von 85° C getrocknet werden. Die mit Bromwasserstoffsäure durchgeführten Bestimmungen gehen schneller und sind vorteilhafter. Die optimalen Bedingungen wurden festgelegt. Es wird eine Methode vorgeschlagen um Gold von den störenden Ionen zu trennen; diese letzteren sind im übrigen nicht zahlreich. Gleichzeitig wird eine Bestimmung von Gold in angereicherten Mineralien beschrieben.

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CHROMATOGRAPHIE SUR PAPIER DES IONS MINÉRAUX

VI. SÉPARATION DES PERCOMPOSÉS DE TITANE, VANADIUM ET MOLYBDÈNE

par

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Parmi les méthodes de séparation par chromatographie du titane et du vanadium, mentionnées dans la littérature[1,2], aucune ne semble convenir pour séparer des traces de vanadium d'avec de grandes quantités de titane.

Dans cette communication nous décrivons une séparation de ces éléments à l'état de percomposés.

La solution de Ti(IV) et V(V) est additionnée d'un excès d'eau oxygénée, puis 0.2 ml environ de mélange sont déposés le long d'une droite sur une feuille de papier d'Arches n° 302. Un développement ascendant d'une durée d'environ 20 heures est effectué avec un solvant, préparé en agitant 10 ml de HCl concentré, 10 ml de H_2O_2 à 30%, 80 ml d'eau et 100 ml de butanol.

Le composé pervanadique forme une bande rouge qui se trouve devant celle qui correspond au composé pertitanique orange, ce qui permet une séparation complète d'environ 2 mg de vanadium d'avec 10 mg de titane sur une seule feuille de papier.

Le molybdène est extrait sous forme d'un percomposé jaune bien avant les deux autres éléments; les valeurs des R_F sont en effet les suivantes: Ti = 0.09; V = 0.27 et Mo = 0.79.

Un certain nombre d'autres éléments ont été chromatographiés avec le solvant utilisé pour cette séparation, Bi, Hg^{+2}, Pb, Co, Ni, Cd, Mn, Cu, Cr, Al, Pd, Rh, Pt, Sb^{+3}, Ag, Sn^{+4}, Ba, Sr, Ce et Th sont tous caractérisés par une valeur de R_F qui est la même que dans le butanol agité avec HCl N[3]. En ce qui concerne Fe^{+3}, son déplacement est légèrement plus rapide (R_F 0.35) lorsqu'il est accompagné de titane. D'autre part l'uranium forme deux taches, une de R_F 0 qui correspondrait au peroxyde insoluble et une autre dont le R_F est celui de UO_2^{+2} dans le mélange butanol HCl (R_F 0.20).

Les percomposés de titane, vanadium et molybdène peuvent aussi être bien séparés par électrophorèse sur papier. En appliquant le technique décrite précédemment[4], on observe, au bout de 50 minutes avec HCl $N/2$ et une tension de 110 volts, un déplacement vers la cathode de 13 mm du titane (bande orange)

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et seulement de 3 mm du vanadium (bande rouge) tandis que le molybdène se déplace vers l'anode de 11 mm (bande jaune). Les trois bandes sont complètement séparées.

RÉSUMÉ

Les percomposés de titane, vanadium et molybdène peuvent être séparés par chromatographie sur papier. On utilise comme solvant un mélange de butanol, HCl, H_2O_2 et eau.

SUMMARY

The percompounds of Ti, V and Mo can be separated by paper chromatography with butanol containing HCl, H_2O_2 and water as solvent.

ZUSAMMENFASSUNG

Die Peroxyverbindungen von Ti, V and Mo können chromatographisch auf Papier mit Hilfe von einer Mischung von Butylalkohol, HCl, H_2O_2 und Wasser getrennt werden.

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ELEKTRONENMIKROSKOPISCHE KONTROLLE DER „WANDWIRKUNG" IN DEN ADSORPTIONSERSCHEINUNGEN

von

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In unserer letzten Arbeit über Adsorptionserscheinungen an den Oberflächen von Silberjodidpartikelchen „in statu nascendi"[1] wurde von uns die Rolle des *p*-Äthoxychrysoidins betreffs Dispersitätsgrad des ausgeschiedenen Silberjodids eingehend besprochen. Es wurde nachgewiesen, dass es für die von uns in Vorschlag gebrachten fällungsanalytischen Titriermethoden[2, 3, 4] entscheidend wichtig ist, dass das, als Adsorptionsindikator wirkende *p*-Äthoxychrysoidin schon gleich beim Anfang des Titrierens vorhanden sei. Das in Gegenwart von *p*-Äthoxychrysoidin entstandene Silberjodidsol besitzt nämlich nach den diesbezüglichen Versuchen auch nach dem Koagulieren eine bedeutend grössere spezifische Oberfläche, als dasjenige, welches ohne *p*-Äthoxychrysoidin hergestellt worden ist[1].

Diese Tatsache, sowie andere, besonders den Ionenaustausch betreffenden Überlegungen, worüber erst nach Beendigung der diesbezüglichen chemischen Versuche berichtet werden soll, veranlassten uns mit dem Elektronenmikroskop zu untersuchen, ob nicht etwaige Unterschiede in der Struktur der Silberjodidpartikelchen nach Verwendung von verschiedenen koagulierenden Mitteln (NH_4NO_3, KNO_3) zu entdecken wären.

Bei diesen Untersuchungen verwendeten wir als Modell—schon aus praktischem Grund—das Silberjodid, da seine von uns näher untersuchten Adsorptionseigenschaften das Prinzip neuer von uns in Vorschlag gebrachter Titriermethoden bildeten.

Schon bei den ersten — allerdings ohne Verwendung von *p*-Äthoxychrysoidin angestellten Versuchen, wo Ammonnitrat, als koagulierendes Mittel verwendet wurde, konnte die Ausbildung einer diffusen Schichte beobachtet werden, welche die Silberjodidpartikelchen schleierartig umhüllte, welche aber auf die Einwirkung von den Elektronenstrahlen mit Augen verfolgbar in wenigen Sekunden verschwand. Die so entstandenen Konturen der Partikelchen waren dann äusserst scharf.

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BESCHREIBUNG DER VERSUCHE

Wir halten es für angezeigt die von uns in den Untersuchungen befolgte Technik genau zu beschrieben. Die Bezeichnungen der, als Beweismaterial dienenden elektronenmikroskopischen Aufnahmen sind mit denen der Beschreibung von den Versuchen identisch.

Die von uns systematisch angestellten Versuche wurden in drei Gruppen folgendermassen ausgeführt.

I. Gruppe. Versuche ohne p-*Äthoxychrysoidin*

1. 1 ml einer 0.01 *M* Silbernitrat-Lösung wurde in einem Messkolben mit 20 ml Wasser, dann mit 0.5 ml einer 0.01 *M* Kaliumjodid-Lösung vermengt, und das Reaktionsgemenge mit Wasser auf 100 ml ergänzt. — Ein Tropfen der opalisierenden Flüssigkeit wird nun auf einer auf ein vergoldetes Kupfernetz für elektronenmikroskopische Zwecke, gebrachten Kollodiummembrane über Blaugel eingetrocknet, endlich unter einem Elektronenmikroskop geprüft, bzw. photographiert.

2. 1 ml einer 0.01 *M* Kaliumjodid-Lösung wurde in einem Messkolben mit 20 ml Wasser, dann mit 0.5 ml einer 0.01 *M* Silbernitrat-Lösung vermengt und weiter genau wie unter 1 verfahren.

3. Es wurde genau, wie unter 1 doch mit dem Unterschied verfahren, dass das Silberjodid vor demVerdünnen auf 100 ml durch Schütteln mit 2.4 g Ammonnitrat koaguliert wurde.

4. Es wurde genau, wie unter 2 doch mit dem Unterschied verfahren, dass das Silberjodid vor dem Verdünnen auf 100 ml durch Schütteln mit 2.4 g Ammonnitrat koaguliert wurde.

5. Es wurde genau, wie unter 1 doch mit dem Unterschied verfahren, dass das Silberjodid vor dem Verdünnen auf 100 ml durch Schütteln mit 1.2 g Kaliumnitrat koaguliert wurde.

6. Es wurde genau, wie unter 2 doch mit dem Unterschied verfahren, dass das Silberjodid vor dem Verdünnen auf 100 ml durch Schütteln, mit 2 g Kaliumnitrat koaguliert wurde.

7. Es wurde genau, wie unter 1 doch mit dem Unterschied verfahren, dass das Silberjodid vor dem Verdünnen auf 100 ml durch Schütteln mit Salpetersäure koaguliert wurde.

8. Es wurde genau, wie unter 5 verfahren. Nach Koagulieren des Silberjodids wurde die Lösung ultrafiltriert. Das, als Objektträger dienende, vergoldete und mit einer Kollodiummembrane überzogene Kupfernetz wurde leicht an den Niederschlag gedrückt, dann in dem Elektronenmikroskop untersucht.

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II. Gruppe. Versuche mit p-Äthoxychrysoidin

9. 1 ml einer 0.01 *M* Silbernitrat-Lösung wurde in einem Messkolben mit 20 ml Wasser, mit 8 Tropfen einer 0.2%-igen, mit 96%-igen Alkohol bereiteten *p*-Äthoxychrysoidin-Lösung, dann mit 0.5 ml einer 0.01 *M* Kaliumjodid-Lösung vermengt.

Das ausgeschiedene Silberjodid wurde durch Schütteln mit 1.2 g Ammonnitrat koaguliert, dann die Flüssigkeit mit Wasser auf 100 ml ergänzt. Es wurde endlich, wie unter 1 angegeben, verfahren.

10. Es wurde genau, wie unter 9 doch mit dem Unterschied verfahren, dass 1 ml 0.01 *M* Kaliumjodid-Lösung mit 0.5 ml 0.01 *M* Silbernitrat-Lösung im Laufe der Untersuchung versetzt wurde.

11. Es wurde genau, wie unter 9 doch mit dem Unterschied verfahren, dass das Silberjodidsol anstatt Ammonnitrats mit 2 g Kaliumnitrat koaguliert wurde.

12. Es wurde genau, wie unter 10 doch mit dem Unterschied verfahren, dass das Silberjodidsol anstatt Ammonnitrats mit 2 g Kaliumnitrat koaguliert wurde.

III. Gruppe. Kontrollversuche

13. Je 1 Tropfen einer reinen 1%-igen Ammonnitrat-Lösung (13a), einer 2%-igen (13b), bzw. 1.2%-igen (13c) Kaliumnitrat-Lösung wurden auf je einer auf ein vergoldetes Kupfernetz gebrachten Kollodiummembrane über Blaugel eingetrocknet und unter dem Elektronenmikroskop untersucht und photographiert.

BESCHREIBUNG DER BEFUNDE

Durch Vergleichung der elektronenmikroskopischen Aufnahmen können folgende von dem angewandten Verfahren bedingten Unterschiede festgestellt werden.

Vergleicht man die Aufnahmen 1 und 2, so findet man, dass die peptisierende Wirkung der Jodidionen auf den Silberjodidniederschlag weitaus grösser, als die der Silberionen ist.

Die schon eingangs erwähnte schleierartige Hülle um die Silberjodidpartikelchen lässt sich auf diesen Aufnahmen gar nicht finden. Bei diesen Versuchen war ja doch weder NH_4NO_3, noch KNO_3, als koagulierendes Mittel verwendet.

Wird das in Abwesenheit von *p*-Äthoxychrysoidin mit Silber- bzw. Jodidüberschuss hergestellte Silberjodidsol nach Koagulieren mit Ammonnitrat unter dem Elektronenmikroskop geprüft (Aufnahmen 3a, 3b und 4), so kann eine die Silberjodidpartikelchen umgebende, schleierartige Hülle beobachtet werden, welche aber durch Einwirkung der Elektronenstrahlen in einigen Sekunden verschwindet. Es sind auf den Aufnahmen 3b und besonders auf 3a, die nachträglich koagulierten Silberjodidpartikelchen ganz augenfällig, die sich in Kreisform geordnet haben. Der im Anfang mit einem Schleier umhüllte Kreis hellte sich infolge Elektronenbestrahlung besonders scharf auf. In dem Versuche 4 (Aufnahme 4) war der Effekt infolge peptisierender Wirkung der überschüssigen

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Jodidionen weniger scharf. Betrachtet man die nach Beschreibung 5 bzw. 6 hergestellten Aufnahmen 5a, 5b, und 6, so sind die die Silberjodidpartikelchen umgebenden diffusen, schleierartigen Hüllen, wenn auch auf der Aufnahme 6, (Jodidüberschuss !) weniger scharf, doch unverfehlbar deutlich zu erkennen. In diesen Versuchen wurde doch das nicht sublimierbare Kaliumnitrat zum Koagulieren verwendet.

In der Aufnahme 7 war keine schleierartige Hülle zu erwarten, da in diesem Versuche (Beschreibung 7) Salpetersäure zum Koagulieren der Silberjodidpartikelchen verwendet wurde.

Prüft man die Aufnahmen 8a, 8b nach der Beschreibung 8 des ultrafiltrierten Silberjodidniederschlages, so findet man die Konturen des zusammengeballten Silberjodids scharf, und von keinem diffusen Schleier begleitet. Dies war übrigens auch zu erwarten.

Die elektronenmikroskopischen Aufnahmen 9a, 9b und 9c, 10a, 10b und 10c gehören zu den Versuchen, in welchen das das Silberjodidsol in Gegenwart von *p*-Äthoxychrysoidin mit Silberüberschuss (Aufnahmen 9a-c), bzw. mit Jodidüberschuss (Aufnahmen 10a-c) nach der Beschreibung 9 bzw. 10 hergestellt wurden. Das Koagulieren wurde in beiden Fällen mittels Ammonnitrats durchgeführt. Wurden die Präparate zur elektronenmikroskopischen Untersuchung gleich nach der Herstellung, d.h. gleich nach dem Eintrocknen der Untersuchungstropfen geprüft, so war eine Schleierbildung immer zu beobachten (Aufnahmen 9a und 10a). Wurden die Präparate erst 6 Tage nach ihrer Herstellung unter das Elektronenmikroskop gestellt, so waren neben der schleierartigen Hülle auch gut entwickelte Ammonnitrat-Krystalle zu finden (Aufnahmen 9b und 9c). Die Form bzw. die Ausbildung der Krystalle war interessanter Weise durch den Einfluss der überschüssigen Jodidionen geändert, bzw. gewissermassen gehindert (Aufnahmen 10b und 10c). Wird das Silberjodidsol mit Kaliumnitrat koaguliert (Aufnahmen 11a, 11b und 12) so entsteht keine schleierartige Hülle. Zwischen den Silberjodidkryställchen lassen sich aber gut entwickelte Kaliumnitrat-Krystalle zu erkennen. Die Struktur des Silberjodids ist infolge Wirkung des *p*-Äthoxychrysoidins[1] in allen Fällen (Aufnahmen 9-12) besonders fein. Die beim Versuche 10b, 10c erwähnte krystalländernde Wirkung des Jodidionenüberschusses kann auch hier (Aufnahme 12) nachgewiesen werden.

Auf den photographischen Aufnahmen 13a, 13b, 13c, der nach Beschreibung 13, ausgeführten Versuche sind — auch von der Temperatur bzw. Konzentrationsverhältnissen bedingt —, verschiedenartige, aber wohl ausgebildete Ammonnitrat (Aufnahme 13a) bzw. Kaliumnitrat (Aufnahmen 13b und 13c) Krystalle zu sehen*. Die Bildung von diffusen schleierartigen Hüllen war in keinem Falle zu beobachten.

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* Eine ähnliche Beobachtung betreffs Ausbildung der Krystallformen wurde von A. Buzágh: *Kolloidik* II/2 360-362, Akademischer Verlag, Budapest 1952 (Ungarisch) beschrieben.

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Fig. 1. AgJ-Sol, mit $Ag^{\cdot}$-Überschuss (Vergr. 20,000 ×)

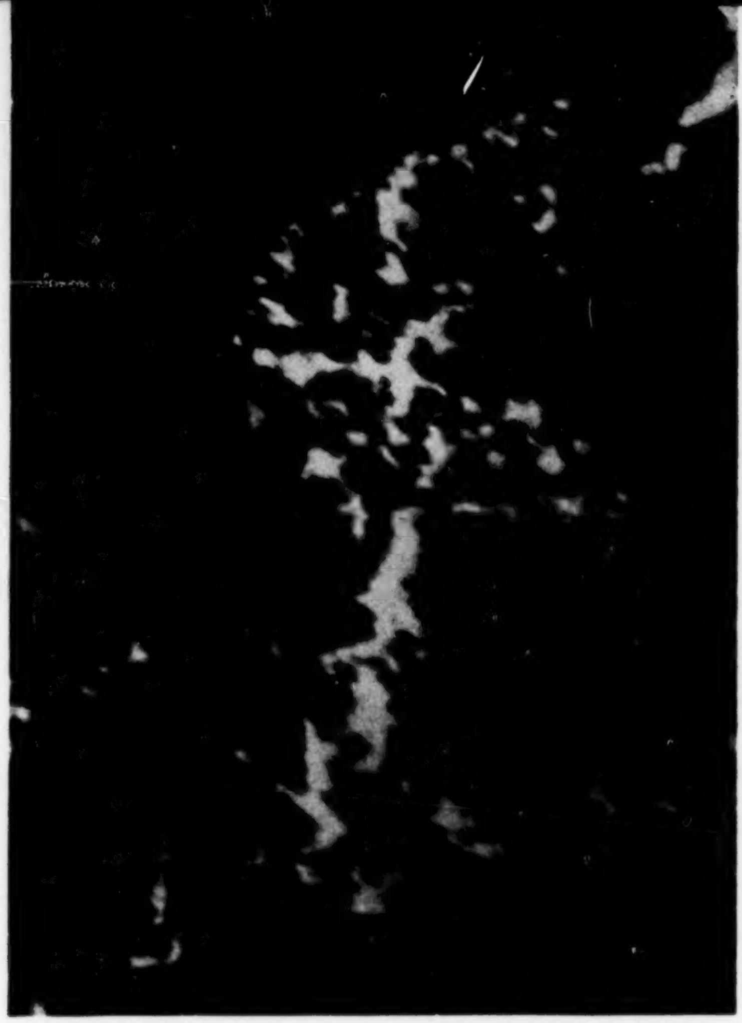


Fig. 2. AgJ-Sol, mit J'-Überschuss (Vergr. 20,000 ×)

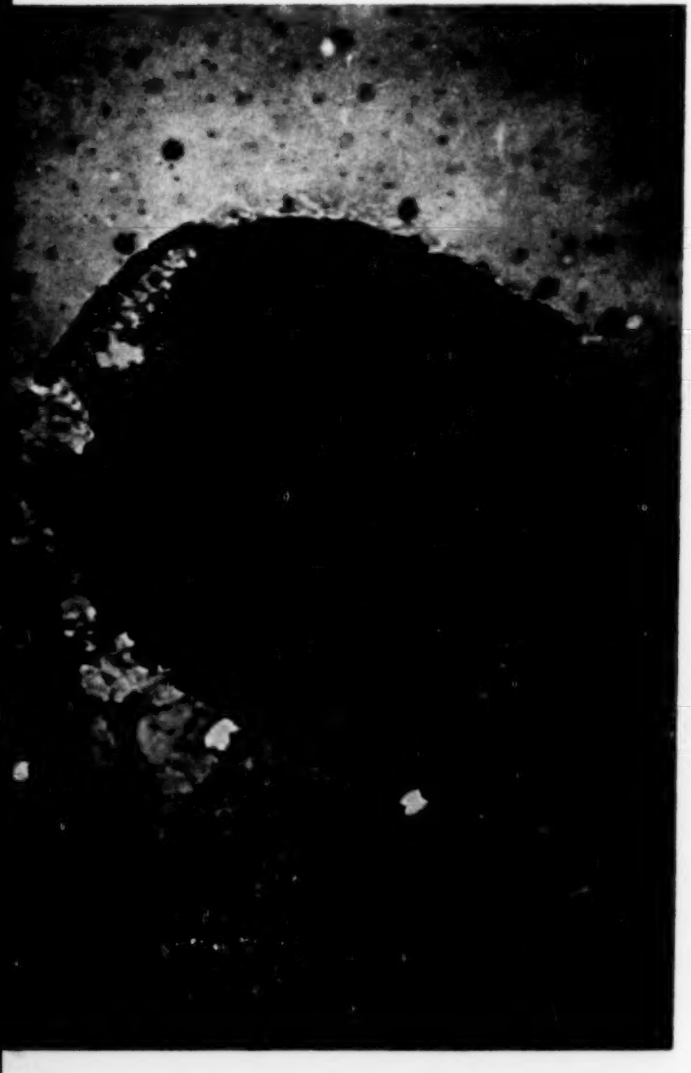


Fig. 3a. AgJ-Sol, mit $Ag^{\cdot}$-Überschuss, aguliert mit NH_4NO_3 (Vergr. 12,000 ×)

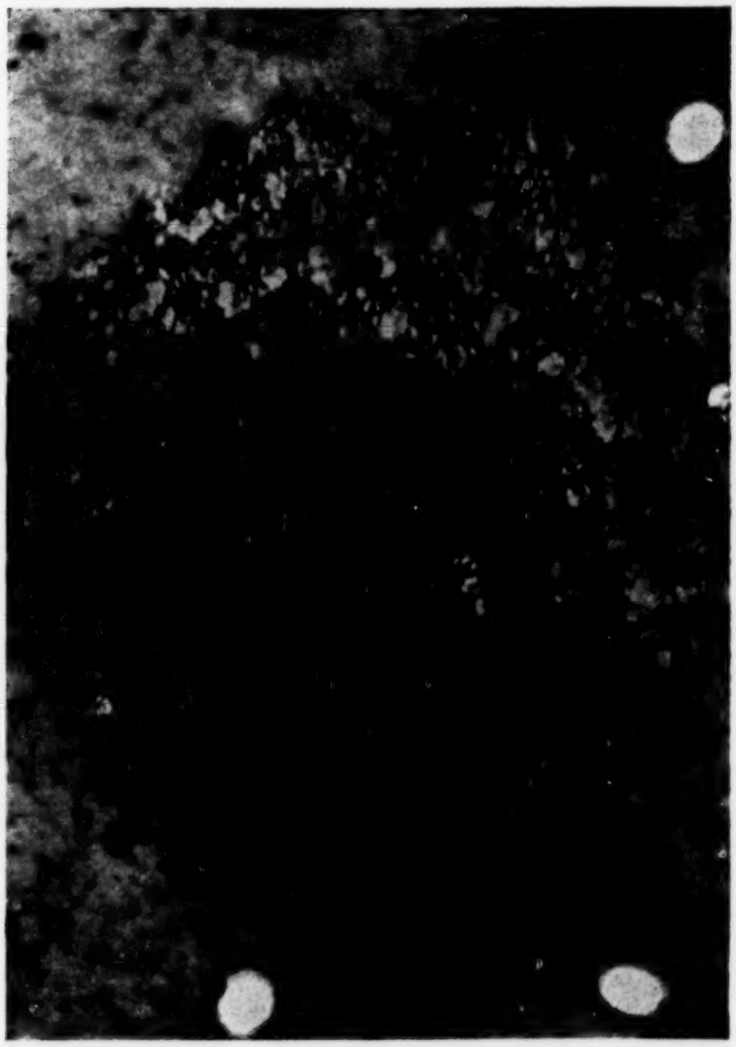


Fig. 3b. AgJ-Sol, mit $Ag^{\cdot}$-Überschuss, koaguliert mit NH_4NO_3 (Vergr. 23,000 ×)

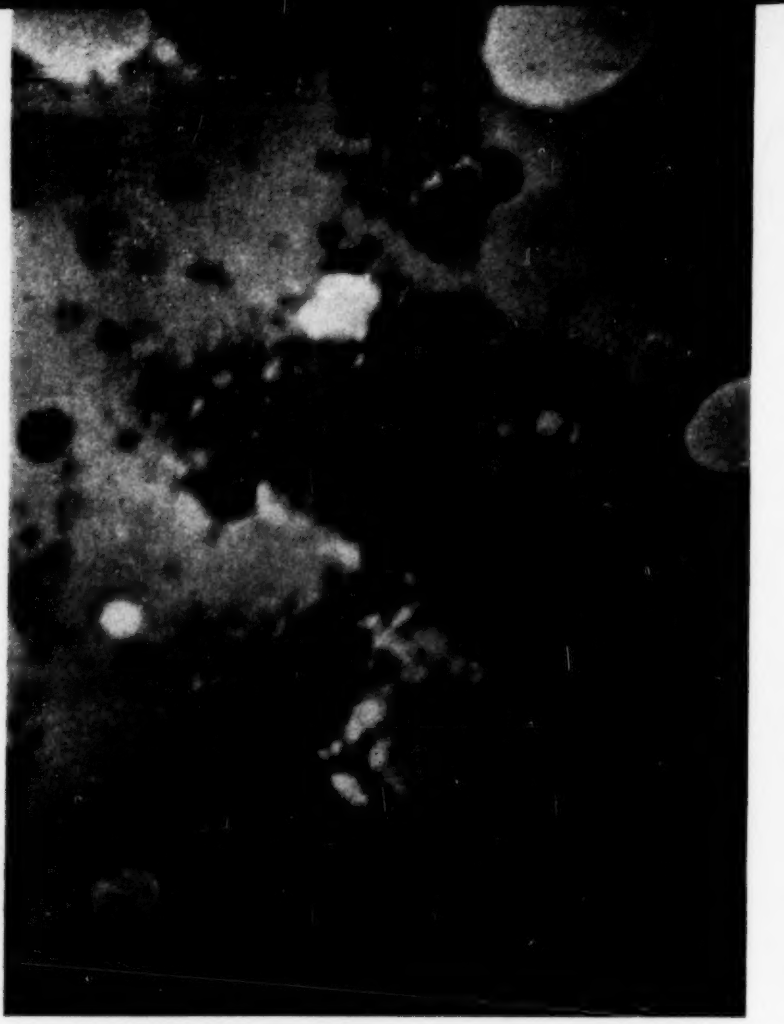


Fig. 4. AgJ-Sol, mit J′-Überschuss, koaguliert mit NH_4NO_3 (Vergr. 7,000)

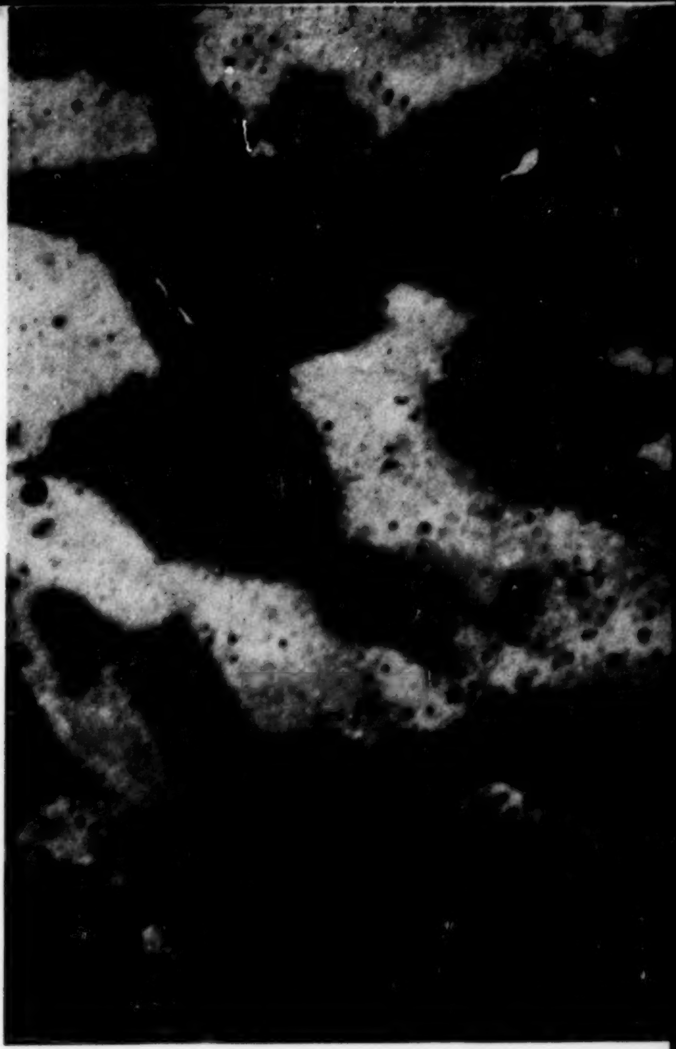


Fig. 5a. AgJ-Sol, mit $Ag^{\cdot}$-Überschuss koaguliert mit KNO_3 (Vergr. 19,000 ×

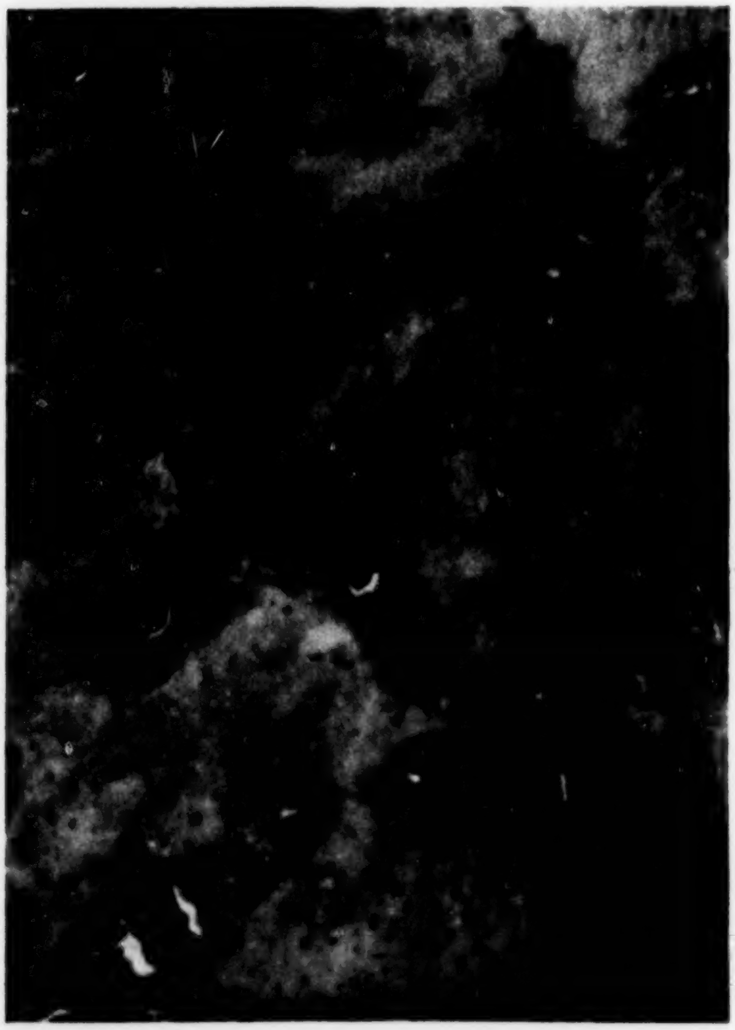


Fig. 5b. AgJ-Sol, mit $Ag^{\cdot}$-Überschuss, koaguliert mit KNO_3 (Vergr. 14,000 ×)

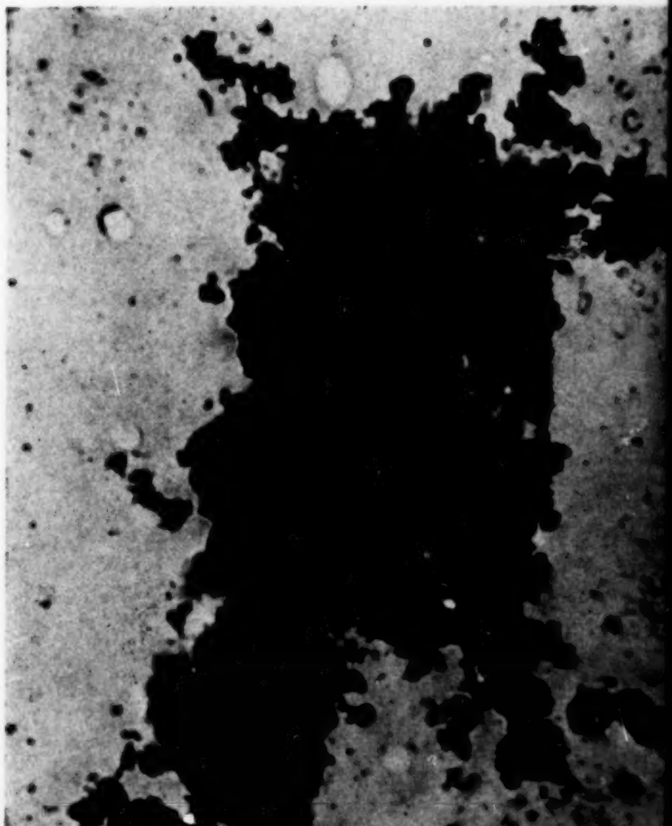


Fig. 6. AgJ-Sol, mit J′-Überschuss, koaguliert mit KNO_3 (Vergr. 13,000 ×

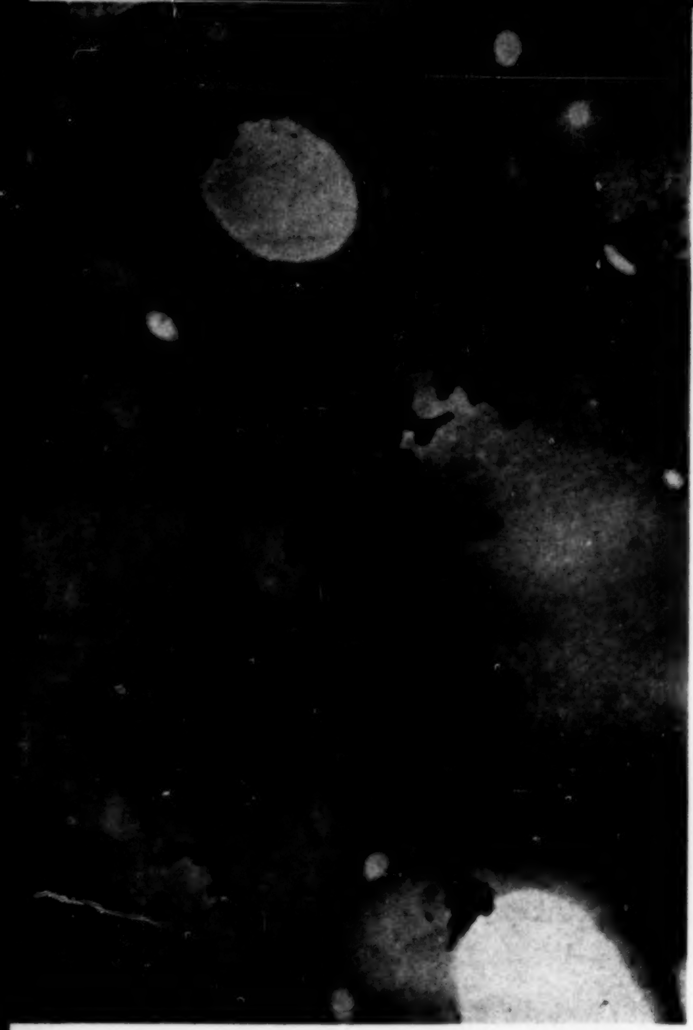


Fig. 7. AgJ-Sol, mit $Ag^{\cdot}$-Überschuss, koaguliert mit KNO_3 (Vergr. 20,000 ×)

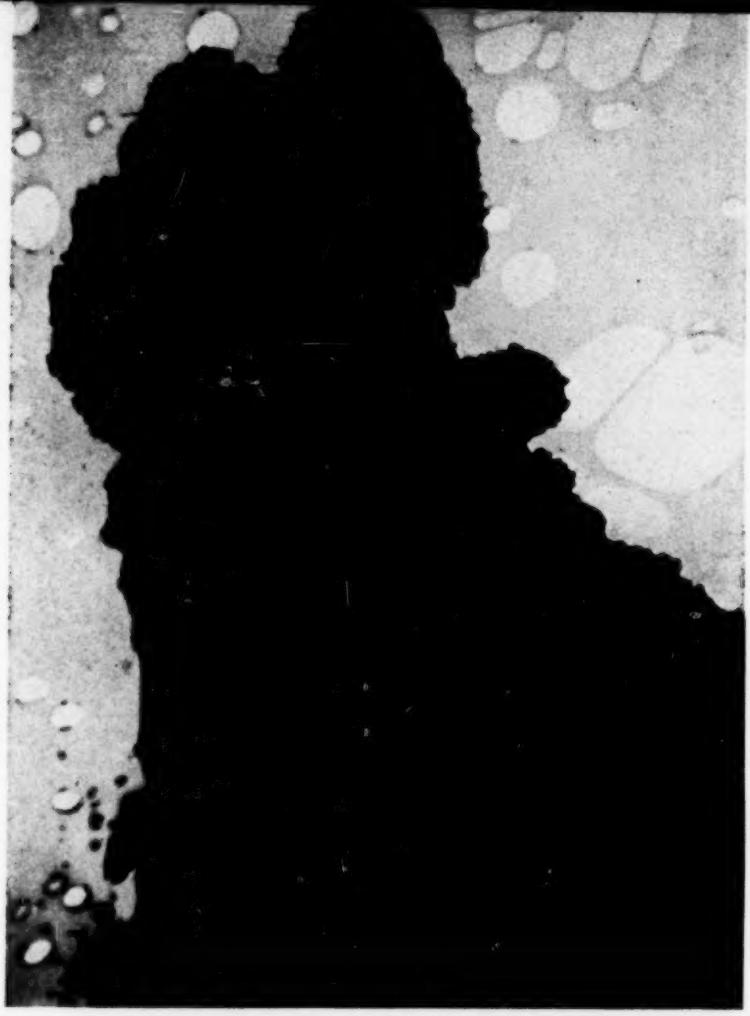


Fig. 8a. AgJ-Sol, mit $Ag^{\cdot}$-Überschuss, koaguliert mit KNO_3 und ultrafiltriert (Vergr. 10,000 ×)

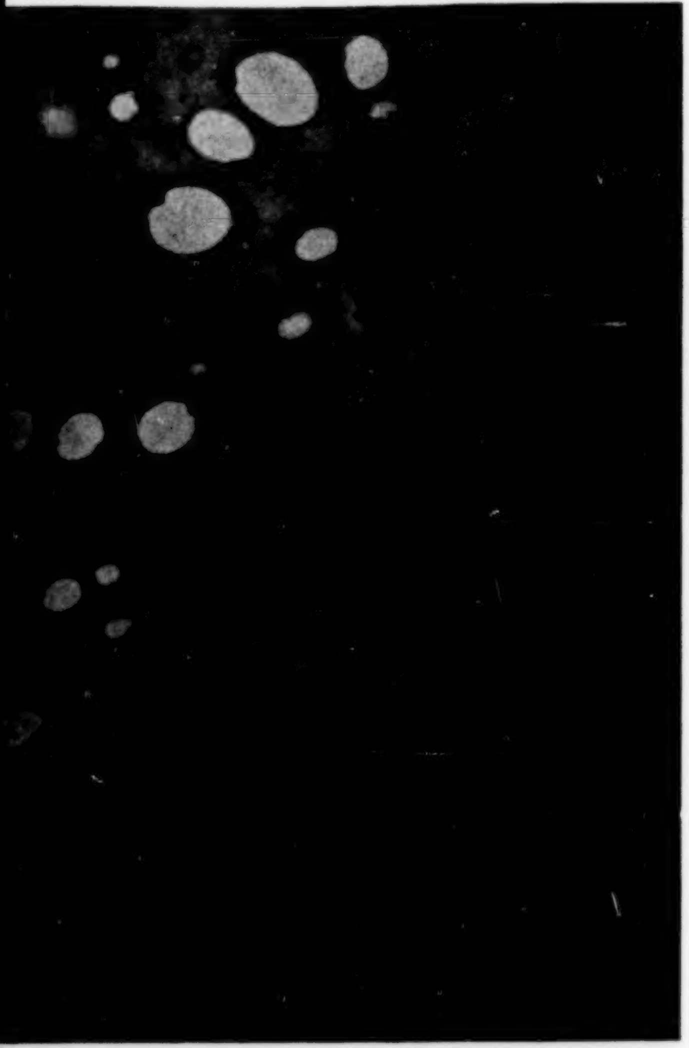


Fig. 8b. AgJ-Sol, mit $Ag^{\cdot}$-Überschuss, koaguliert mit KNO_3 und ultrafiltriert (Vergr. 10,000 ×)

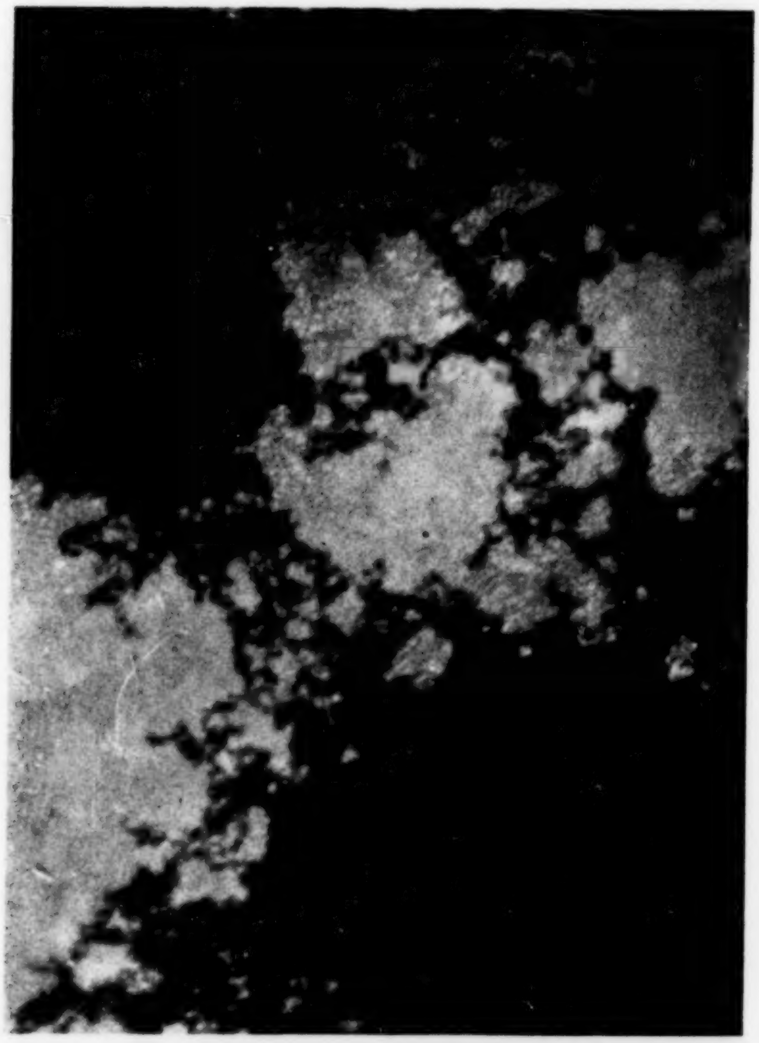


Fig. 9a. AgJ-Chrysoidin-Sol, mit $Ag^{\cdot}$-Überschuss, koaguliert mit NH_4NO_3, sofort geprüft (Vergr. 14,000 ×)

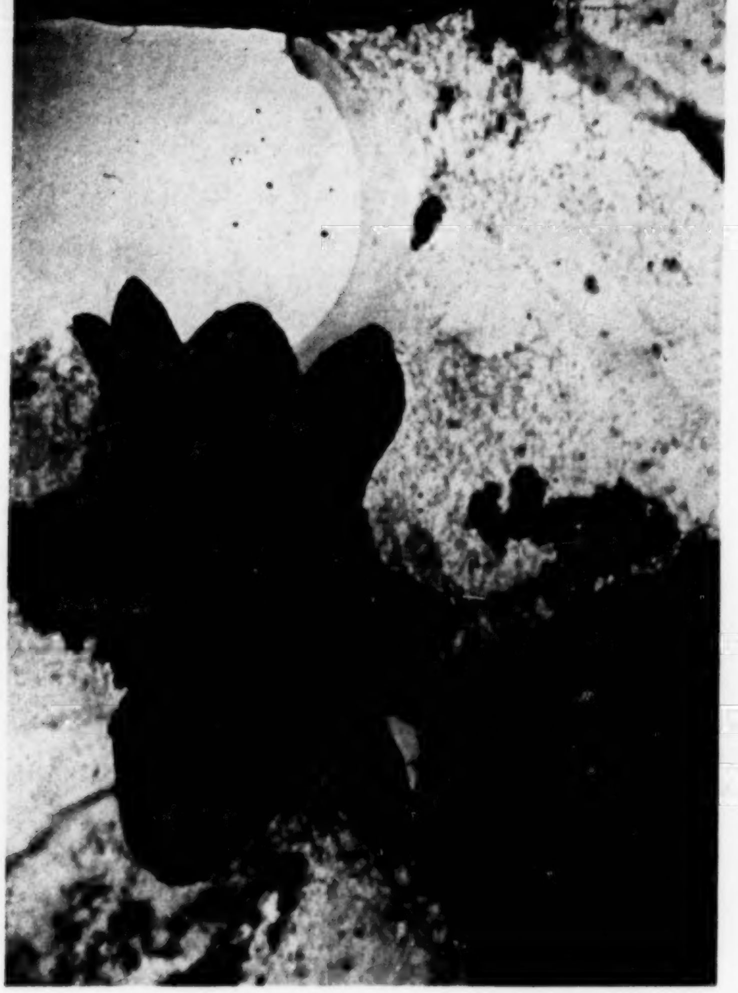


Fig. 9b. AgJ-Chrysoidin-Sol, mit $Ag^{\cdot}$-Überschuss, koaguliert mit NH_4NO_3, nach 6 Tagen geprüft (Vergr. 9,000 ×)

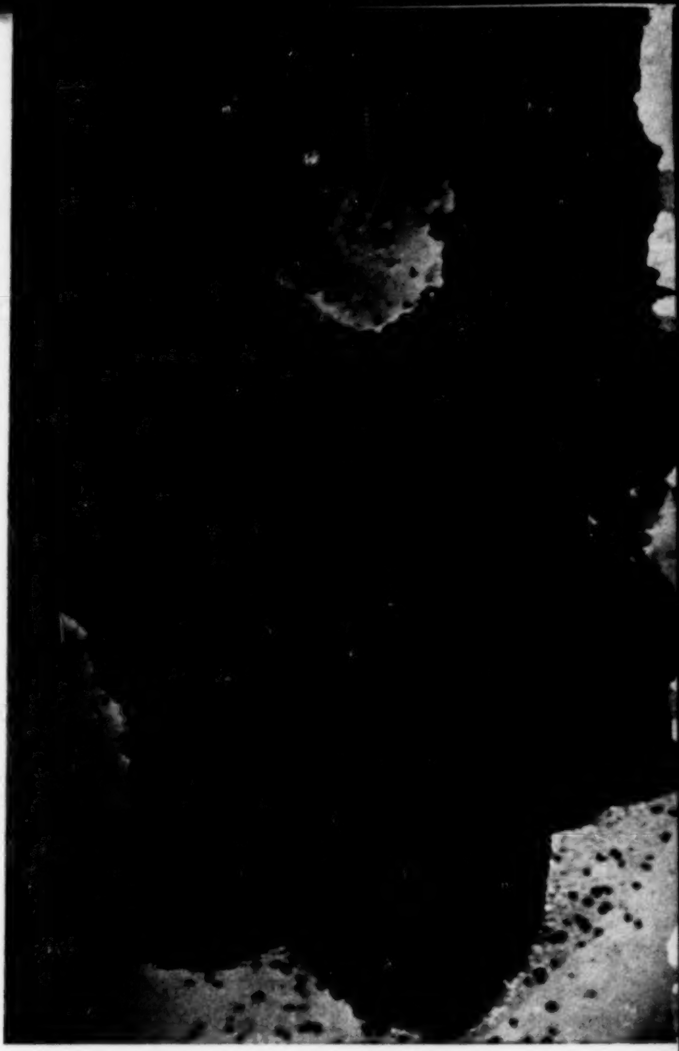


Fig. 9c. AgJ-Chrysoidin-Sol, mit $Ag^{\cdot}$-Übe schuss, koaguliert mit NH_4NO_3, nach 6 Tagen geprüft (Vergr. 8,000 ×)

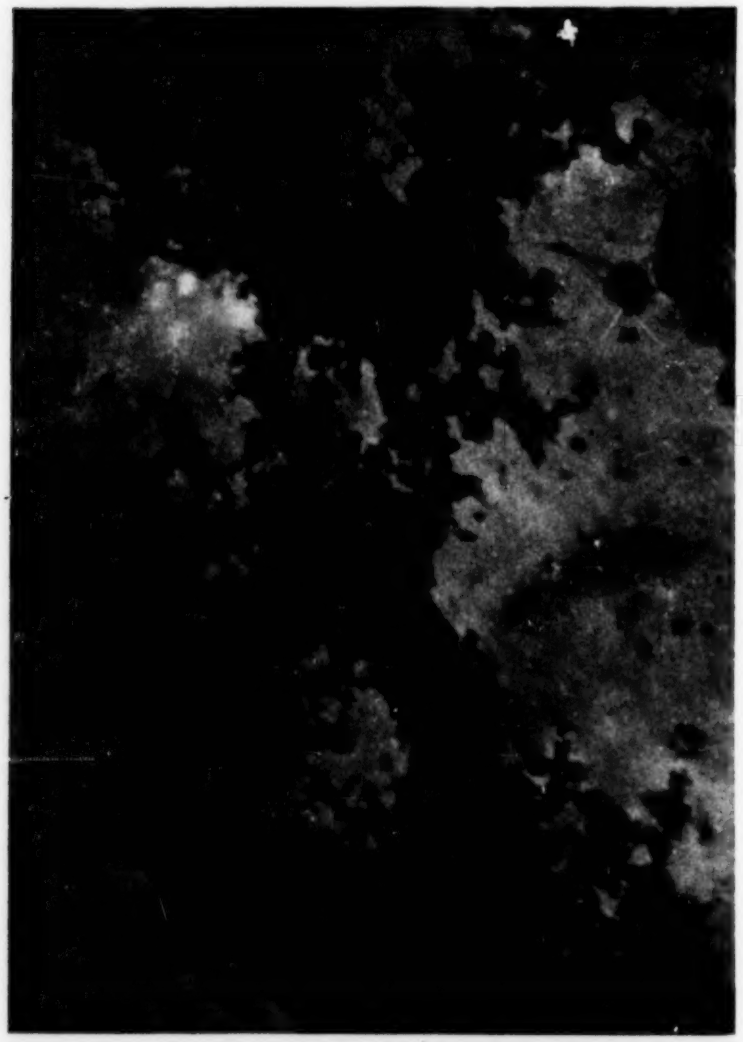
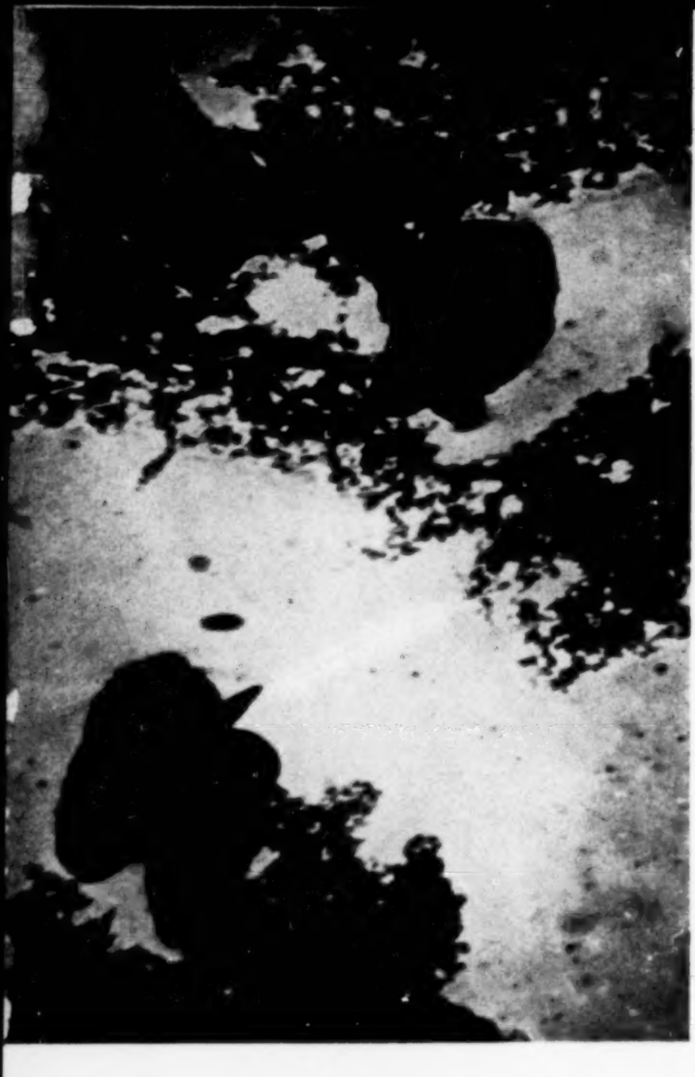


Fig. 10a. AgJ-Chrysoidin-Sol, mit J'-Überschuss, koaguliert mit NH_4NO_3, sofort geprüft (Vergr. 14,000 ×)

Fig. 10b. AgJ-Chrysoidin-Sol, mit J'-Übe schuss, koaguliert mit NH_4NO_3, nach 6 Tagen geprüft (Vergr. 8,000 ×)



ig. 10c. AgJ-Chrysoidin-Sol, mit J'-Überschuss, koaguliert mit NH_4NO_3, nach 6 Tagen geprüft (Vergr. 10,000 ×)

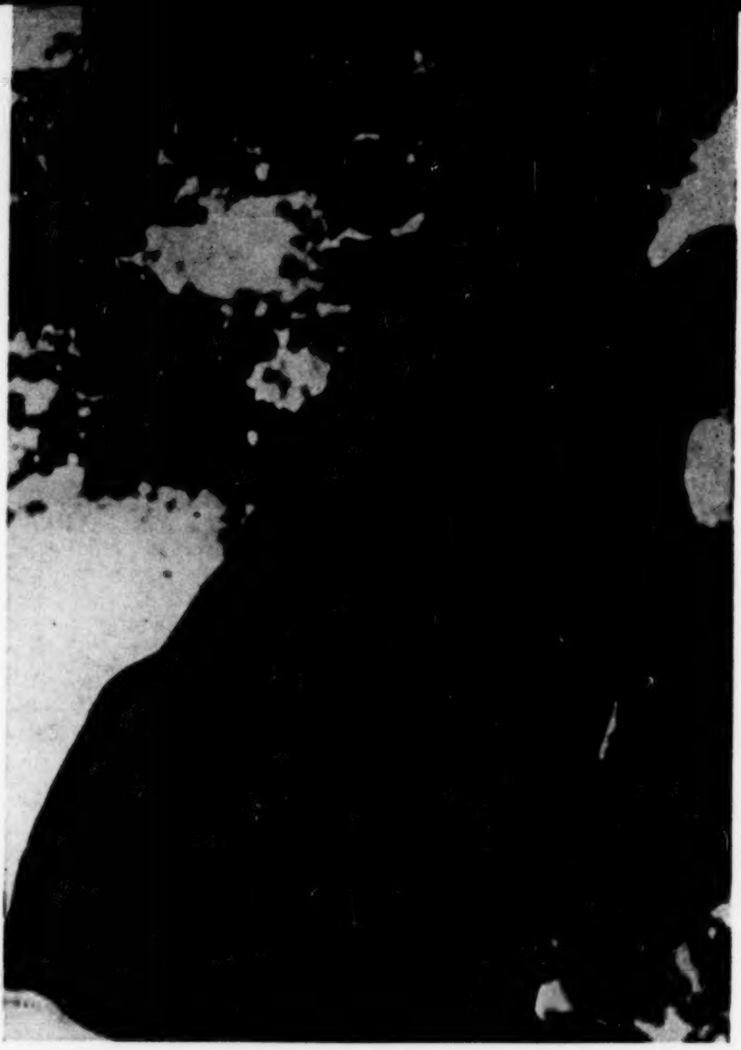


Fig. 11a. AgJ-Chrysoidin-Sol, mit $Ag^{\cdot}$-Überschuss, koaguliert mit KNO_3 (Vergr. 10,000 ×)

ig. 11b. AgJ-Chrysoidin-Sol, mit $Ag^{\cdot}$-Über
uss, koaguliert mit KNO_3 (Vergr. 21,000 ×)

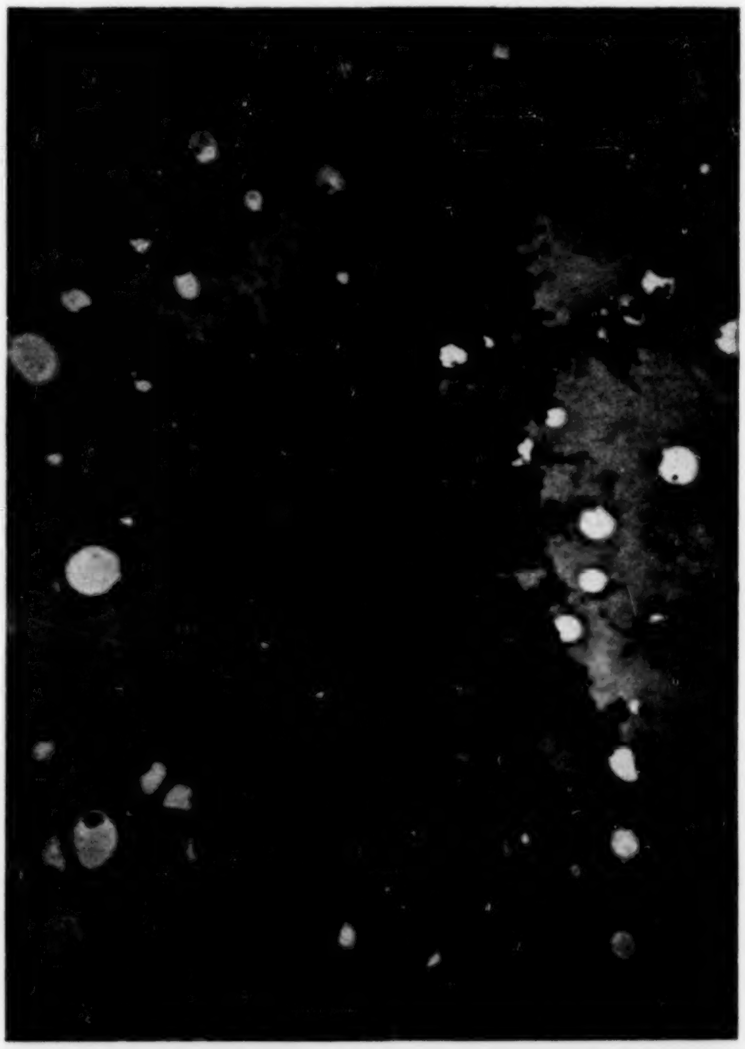


Fig. 12. AgJ-Chrysoidin-Sol, mit J'-Überschuss, koaguliert mit KNO_3 (Vergr. 12,000 ×)

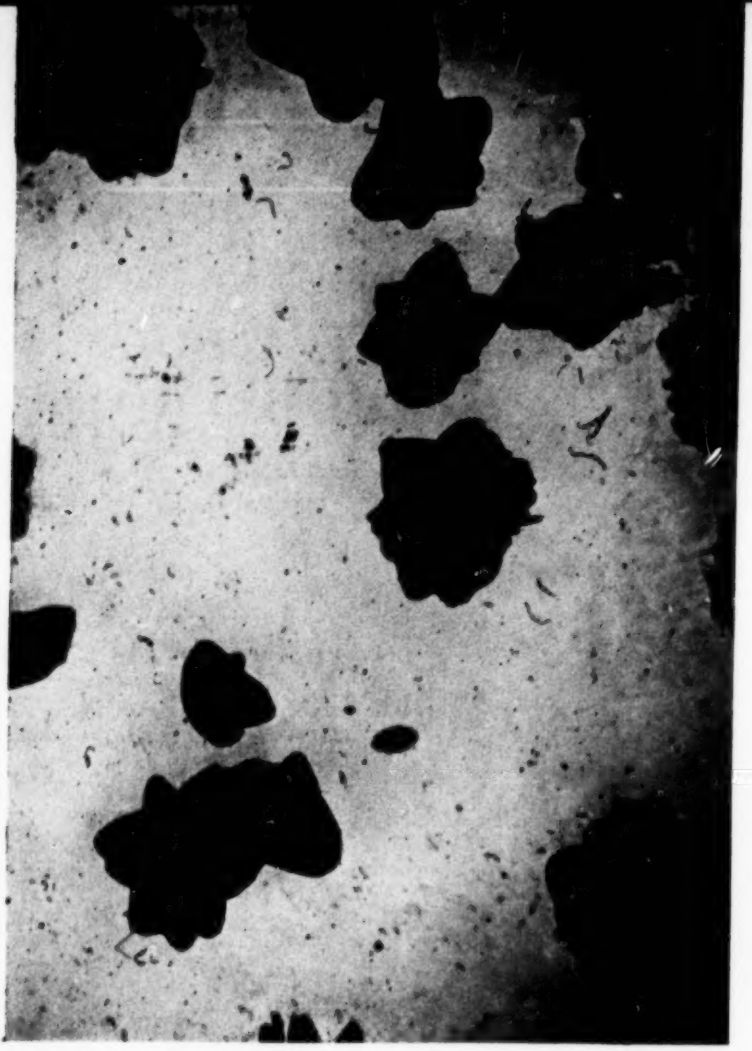


Fig. 13a. NH_4NO_3-Kristalle (Vergr. 5,000 ×)

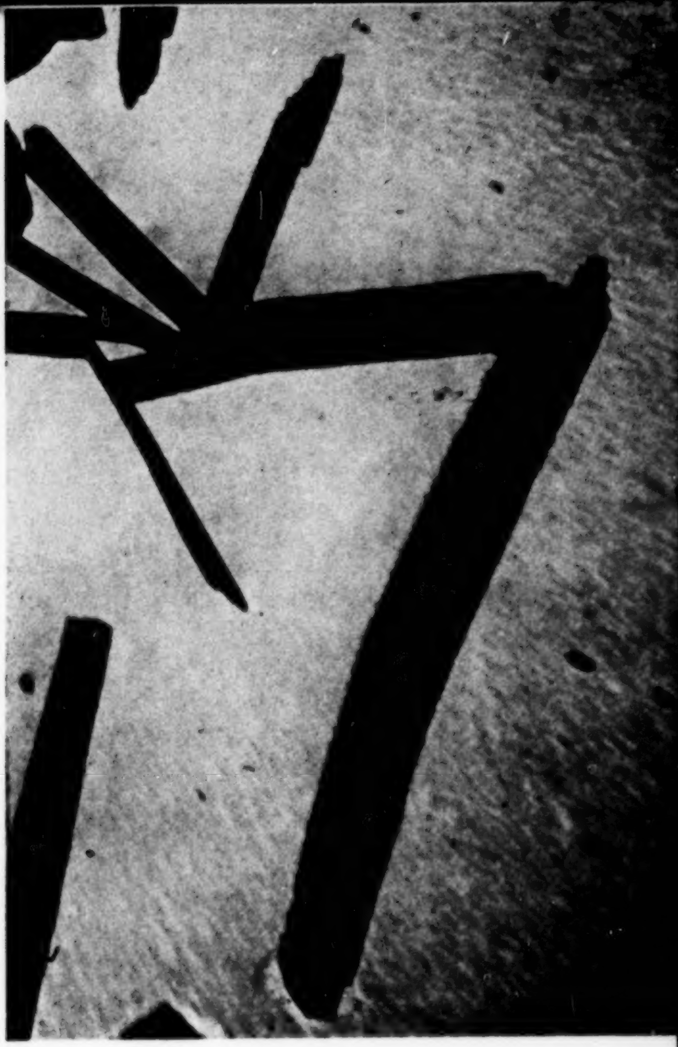


Fig. 13b. KNO_3-Kristalle (Vergr. 12,000

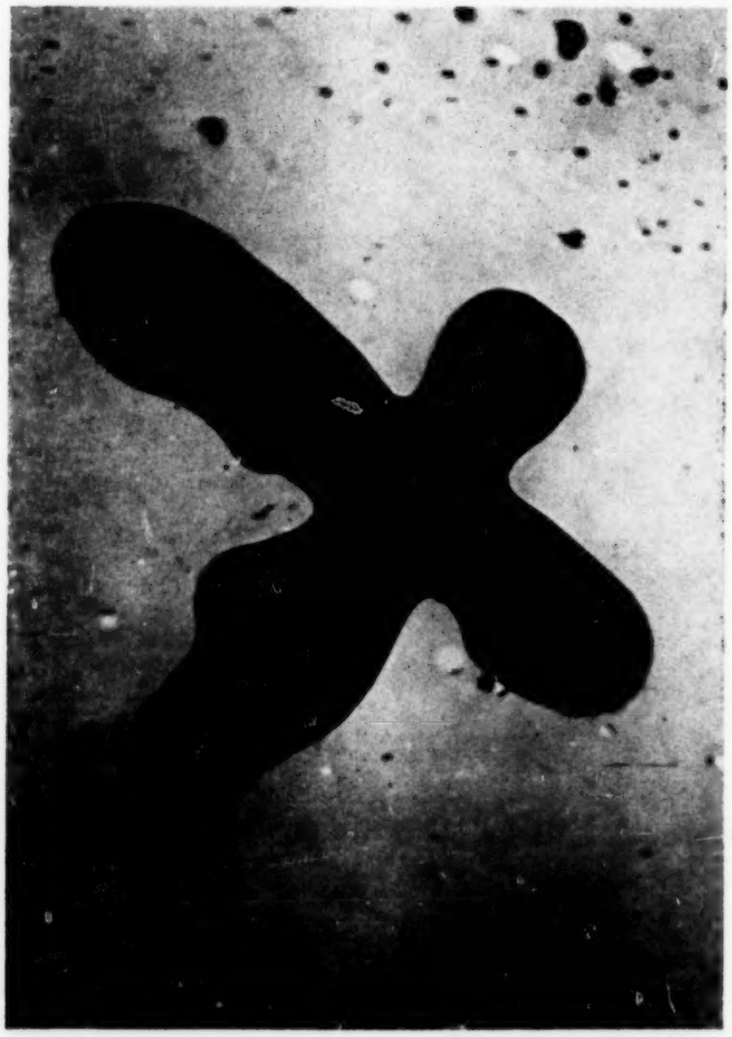


Fig. 13c. KNO_3-Kristalle (Vergr. 14,000 ×)

BESPRECHUNG DER RESULTATE

Das Erklären der beschriebenen Erscheinungen stiess anfangs auf Schwierigkeiten. Die Bildung der diffusen schleierartigen Hülle um die Silberjodidpartikelchen konnte mit der direkten Auswirkung der Adsorptionskräfte um so weniger gedeutet werden, da eine auf 100-500 mμ reichende Tragweite dieser Kräfte nicht vorausgesetzt werden konnte.

Die um die Silberjodidpartikelchen gebildete schleierartige Hülle kann nur als aus dem—als koagulierendes Mittel verwendeten—Ammonnitrat herrührend betrachtet werden, da diese Hülle eben durch die Einwirkung der Elektronenstrahlen mit Leichtigkeit in einigen Sekunden verschwindet (Aufnahmen 3a und 3b), obwohl eine solche Hülle bei der Ausbildung von Ammonnitratkrystallen (Aufnahme 13a) nicht zu beobachten war. Aber auch die Ammonnitratkrystalle konnten mit Elektronenstrahlen nicht verflüchtigt werden. Eine ganz ähnliche Erscheinung war auch dann zu beobachten, wenn Kaliumnitrat anstatt Ammonnitrat zum Koagulieren des Silberjodidsols verwendet wurde. Doch war der die Silberjodidpartikelchen umhüllende Schleier nicht sublimierbar (Aufnahmen 5a-b und c).

Als auffallend muss noch die Tatsache bezeichnet werden, dass die Hülle in keinem Falle eine krystalline Struktur besass. Der die Silberjodidpartikelchen als Keime umhüllende Schleier sollte demnach einen ganz eigenartigen Aufbau haben. Die Schleierbildung ist allerdings statistisch, da auch Silberjodidpartikelchen ohne Hülle vorzufinden sind.

Nach anderen elektrochemischen Versuchen, über welche demnächst zu berichten beabsichtigt wird, können die Silberjodidpartikelchen unter bestimmten Verhältnissen aus der nitrathaltigen Lösung Salpetersäure an ihre Oberfläche adsorbieren. Die adsorbierte Schichte erreicht nach annähernder Berechnung eine Dicke von etwa 10 Molekülen. In Anbetracht dieser Befunde kann man sich die Entstehung der die Silberjodidpartikelchen umgebenden schleierartigen Hülle folgendermassem vorstellen.

Die schleierartig ausgebildete Kaliumnitrat- bzw. Ammonnitrat-Hülle ist ein durch Eindampfen des kalium- bzw. ammonnitrathaltigen Silberjodidsols entstandenes Koagulum von amorpher Struktur. Beim ultrafiltrierten Niederschlag — da in diesem Falle kein Eintrocknen stattfand — war keine Schleierbildung zu beobachten. Beim Eintrocknen des kalium- bzw. ammonnitrathaltigen Silberjodidsols werden die Lösungen an Kalium- bzw. Ammonnitrat übersättigt, gleichzeitig üben die Silberjodidkryställchen eine Keimwirkung aus. Da nun aber die Silberjodidpartikelchen infolge von Adsorptionskräften mit Salpetersäuremolekeln, bzw. aus solchen Molekeln bestehenden, auswärts gerichteten Ketten bedeckt sind, in derem Kraftfeld sich das Kalium- bzw. Ammonnitrat in entsprechender Krystallform nicht ausscheiden resp. ausbilden kann, entsteht das amorphe Koagulum. In diesem Koagulum sind nun die die Molekeln zusammen-

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haltenden Kräfte, wie bekannt, viel kleiner, als in den Krystallen. Dieser Umstand hat nun zur Folge, dass die schleierartig amorph ausgeschiedene Ammonnitrathülle im Gegensatz zu den Ammonnitratkrystallen, sowie zur amorphen Kaliumnitrathülle durch Einwirkung der Elektronenstrahlen zum Wegsublimieren im Stande war.

Die Art der Ausbildung einer schleierartigen Hülle in Gegenwart von *p*-Äthoxychrysoidin kann man sich nach dem in Fig. 14 angegebenen Schema vorstellen. Die durch die Einwirkung der Adsorptionskräfte als Dipole geordneten Salpetersäuremoleküle bedingen die Struktur der Hülle.

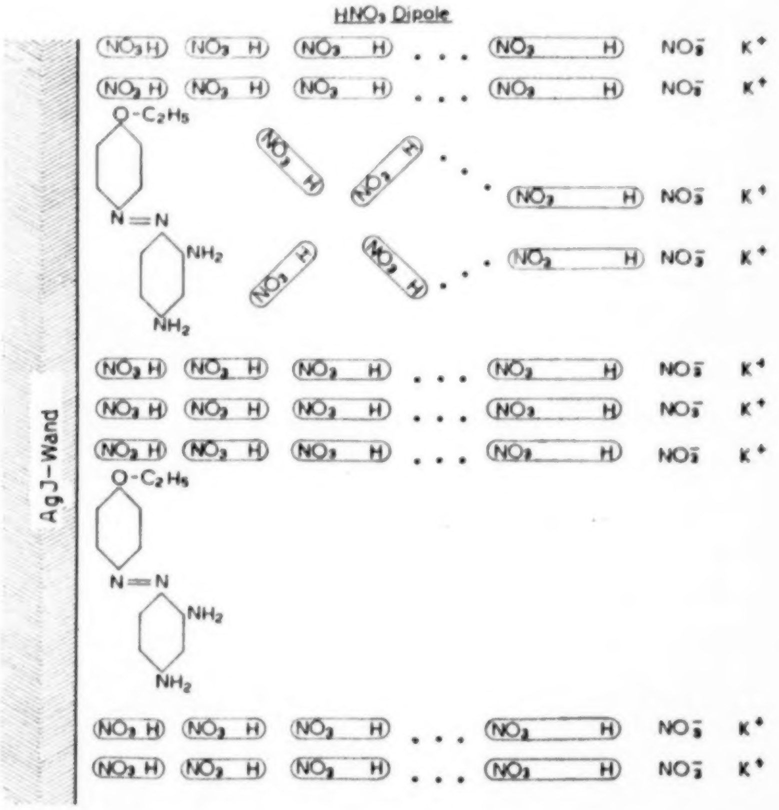

Fig. 14

Besonders interessant ist nun der Befund, dass es aus dem amorphen Koagulum, das sich, als schleierartige Hülle, um die Silberjodidpartikelchen ausscheidet, wenn das in Gegenwart von *p*-Äthoxychrysoidin hergestellte Silberjodidsol mit Ammonnitrat koaguliert war, Ammonnitrat-Krystallkeime ausbilden können. Die Krystallbildung selbst stellt aber einen langsamen Vorgang dar. Die Keimbildung befindet sich nur an einigen Stellen der mit *p*-Äthoxychrysoidinmolekeln bedeckten Silberjodidoberfläche*, da die aus Salpetersäuremolekeln bestehenden auswärts gerichteten Ketten auch an den mit Farbstoffmolekeln bedeckten Plätzen der Oberfläche ihre hemmende Wirkung auf die Keimbildung ausüben.

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* Nach unserer Beurteilung ein besonders wichtiger Umstand in der Bildung von grossen Krystallen!

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Es ist weiter noch zu bemerken, dass die Formbildung der Krystalle scheinbar der eigenartigen Einwirkung der anwesenden bzw. der adsorbierten Eigenionen im Krystallkeim zugeschrieben werden müssen.

Die Tatsache, dass die Bildung der schleierartigen Hülle in den Versuchen mit in Gegenwart von *p*-Äthoxychrysoidin hergestelltem und mit Kaliumnitrat koaguliertem Silberjodidsol ausbleibt, kann damit erklärt werden, dass sich die Kaliumnitratkrystalle mit grösserer Wachstumsgeschwindigkeit, als die Ammonnitratkrystalle ausbilden können. Die kettenartige Ausbildung der Salpetersäure-Dipole bleibt allerdings unverändert, wie das im Falle von Ammonnitrat beschrieben ist. Dies hat nun zur Folge, dass in letzterem Falle, auf den Aufnahmen 9-11 gut ausgebildete Ammonnitrat- bzw. Kaliumnitratkrystalle zwischen den Silberjodidpartikelchen vorzufinden sind.

Wir wollen nicht versäumen, Herrn S. ROHRSETZER für seine Hilfe beim Ultrafiltrieren, sowie Herrn J. KÉTHELYI für die tatkräftige Mitwirkung bei der Ausführung der Analysen zu danken.

ZUSAMMENFASSUNG

Wird ein Silberjodidsol mit Ammonium- bzw. Kaliumnitrat koaguliert und ein Tropfen der noch opalisierenden Lösung eingetrocknet unter dem Elektronenmikroskop untersucht, so kann eine die Silberjodidpartikelchen umgebende schleierartige Hülle beobachtet werden, welche im Falle von Ammonnitrat durch Einwirkung der Elektronenstrahlen in einigen Sekunden verschwindet. — Die Erscheinung und ihre Erklärungsmöglichkeit wird näher besprochen.

SUMMARY

When a sol of silver iodide is coagulated by means of ammonium or potassium nitrate and a drop of the still opalescent liquid is examined under the electron microscope, the formation of an envelope around the silver iodide particles is observed. This envelope disappears in a few seconds, in the presence of ammonium nitrate, under the influence of electron rays. The explanation of this phenomenon is discussed.

RÉSUMÉ

Lorsqu'on coagule un sol d'iodure d'argent, au moyen de nitrate d'ammonium ou de potassium et qu'on évapore à sec une goutte de la liqueur encore opalescente, au microscope électronique, on observe la formation d'une espèce d'enveloppe autour des petites particules d'iodure d'argent; cette enveloppe disparaît en quelques secondes, en présence de nitrate d'ammonium, sous l'influence des faisceaux d'électrons. L'explication de ce phénomène est discutée.

LITERATUR

[1] E. SCHULEK UND E. PUNGOR, *Anal. Chim. Acta*, 7 (1952) 243.
[2] E. SCHULEK UND E. PUNGOR, *Anal. Chim. Acta*, 4 (1950) 109.
[3] E. SCHULEK UND E. PUNGOR, *Anal. Chim. Acta*, 4 (1950) 213.
[4] E. SCHULEK UND E. PUNGOR, *Anal. Chim. Acta*, 5 (1951) 422.

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SPECTROCHEMICAL COBALT, MOLYBDENUM AND COPPER DETERMINATIONS IN PLANTS

by

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I. INTRODUCTION

Spectrochemical analysis is one of the few possible methods for determining trace elements in plant samples, and in other biological material, soils and soil extracts, etc. In this paper the elements considered are restricted to Co, Mo and Cu, which elements are present in oven dry plant material for about $5 \cdot 10^{-5}$, $2 \cdot 10^{-4}$ and $10^{-3}\%$ respectively. The analysis method dealt with may also be used for the other enumerated kinds of samples and as a general method regarding elements and samples. It has been extensively treated elsewhere[1]. In many aspects the pioneering work of MITCHELL c.s. was followed [2, 12, 13, 14]. Additional and differing aspects will be treated below.

II. LIGHT SOURCE, OPTICS AND METHOD OF INTENSITY MEASUREMENT

1. Light source

After a suitable pretreatment (see III) the content of the concerned elements in the sample amounts to about $10^{-2}\%$ (except for a case touched in III. 4).

It has been checked that only the carbon arc cathode layer [3, 4] and the so-called "high voltage a.c. arc*" [5, 6] — which essentially is a cathode layer arc over its whole length — possess a sufficient sensitivity for an accurate trace element determination in the content range concerned. This sufficient sensitivity arises from the favourable line to background ratio in the spectrum of the cathode layer light. In the experiments for the carbon arc cathode layer the sample was introduced in the hollow, lower electrode as a dry powder; for the high voltage arc the sample was present as a thin film of salts after evaporation of a solution on the top of the flat lower electrode.

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* It had better be called "small electrode distance arc".

As the result of the orientation the carbon arc cathode layer has been preferred for its simpler design, while it is also less dangerous in handling. For details of the arc arrangement literature[1,2] may be consulted.

2. *Spectral apparatus*

As a spectral apparatus a Hilger Large Quartz spectrograph was applied. Because of its high resolving power the favourable line to background ratio of the carbon arc cathode layer is well retained. A high resolving power is desirable because many iron spectral lines are present, coming from some percents of iron in the pretreated sample (see III).

A prism spectrograph is more preferable than a grating spectrograph for its great luminosity. In a provisional experiment the estimative luminosity ratio of a large prism and a 2 m grating spectrograph appeared to be *ca.* 50 (the surfaces of the side wall of the prism and of the grating were 50 and 20 square cm respectively).

A quantitative analysis has been carried out of the influence of temperature on the adjustment of a large size Littrow type spectrograph. It showed that the only significant change in adjustment is caused by two effects in the quartz prism. Firstly, the refractive index is dependent on temperature and, secondly, the refracting angle decreases at increasing temperature because of the anisotropy of quartz. These effects result in a shift of the spectral line of *ca.* 0.005 cm/°C. The theoretical line halfwidth on the plate amounts to *ca.* 0.003 cm. Comparison of both values shows that the effect is troublesome for photographic work with very long exposures and for series of photoelectric measurements, unless the temperature is kept constant.

3. *Optics*

To separate the cathode-layer light from the light emitted by the rest of the discharge the arc was larger imaged on a diaphragm. To have a short light path we have erected that diaphragm inside the spectrograph. In this way the required homogeneous slit illumination (see II. 4) is obtained simultaneously.

It must be noted that a homogeneous slit illumination does not always give the wanted homogeneous spectral line on the plate*. The homogeneous line is only obtained when the light of the separated layer entering the slit is nowhere in the spectrograph prevented in reaching the plate**. For this purpose it was thought preferable to erect in the used Littrow type spectrograph the previously mentioned diaphragm just before the prism side wall and not before the collimator lens. An auxiliary diaphragm may be present on the lens to avoid unwanted reflection light; its opening, however, must be so large that it does not limit the light path.

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* A spectral line is called homogeneous when the (maximum) photometric density of the photographed line is independent of the place in the longitudinal direction of the line.

** An inevitable loss in light as a consequence of reflection at the quartz surfaces is left out of account.

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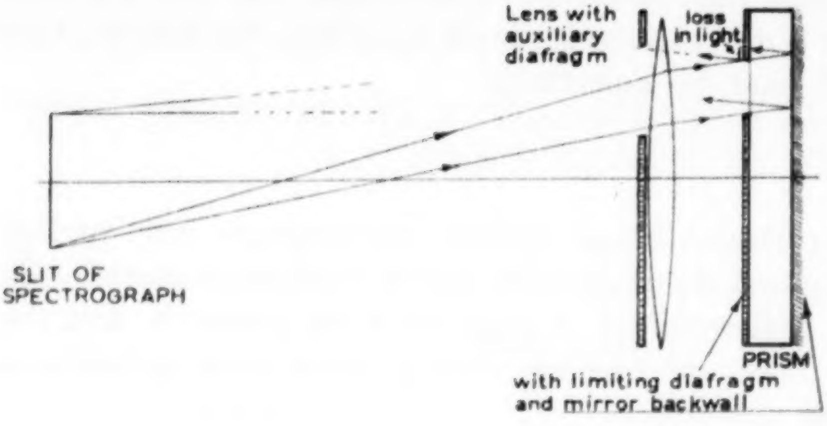
Lens with auxiliary diafragm
loss in light
SLIT OF SPECTROGRAPH
PRISM
with limiting diafragm and mirror backwall

Fig. 1. Showing an exaggeration of the inevitable (minimum) loss in light when the diaphragm is erected just in front of the prism.

When all mentioned points are observed a small inevitable inhomogeneity remains in the line on the plate. It arises from the fact that in a Littrow type spectrograph the light passes in its forward and backward way the diaphragm limiting the light path. The diaphragm cannot coïncide with the mirror behind the prism and therefore prevents a part of the light, reflected by the mirror, from reaching the plate, as it is illustrated in Fig. 1.

The deviation from homogeneity can be calculated and measured. When the height of the opening in the diaphragm is 1 cm, the deviation amounts to about 3% when this limiting diaphragm is erected in front of the prism. The deviation increases when the mentioned diaphragm is more removed from the mirror back wall of the prism, *e.g.* it amounts to about 10% when the diaphragm is erected in front of the collimator lens.

It is desirable to have the homogeneity of the spectral line checked at intervals, since it may be disturbed by small disarrangements in the optics and the slit of the spectrograph.

When a spectral region of larger extent (*e.g.* 1000 A) is observed, an achromatic lens is required for the focussing of the source on the diaphragm. This image must be very sharp, otherwise errors far beyond the mean error of the method (see IV. 3) are introduced, at any rate in the case of a very inhomogeneous light source as a cathode layer*. It is not necessary to place this imaging lens just in front of the spectrograph slit. This is even undesirable when the lens shows small irregularities, as a quartz-fluorite achromatic lens often does.

4. Plate calibration

It was convenient to start the research with the photographic plate as a detector. A photoelectric measurement method is in preparation now[7].

In agreement with MITCHELL c.s.[2] the blackening curve separation method[8,9] has been chosen for the determination of relative intensities in the spectrum.

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* Quantitative data: page 59 of the first reference.

This method was preferred in our case to the method of the precalibrated iron lines[10] and the line width method[11]. Other methods were not to be considered.

The choice of the method of the blackening curve separation implies the requirement of a homogeneous illumination of the slit, in front of which a rotating step sector has been placed.

In the plate choice a great number of considerations play their part (*e.g.* desirable three minutes exposure time given by complete evaporation of the sample, luminosity of spectrograph after diaphragmation, trace element content range to be considered, etc.). It was a lucky chance that all the requirements could be met by application of a usual plate (*e.g.* Gevaert Normal or Ilford Special Rapid).

III. CHEMICAL PRETREATMENT

1. Scopes of pretreatment

For biological samples it is necessary in most cases to apply a pretreatment to obtain the material in a suitable state for spectrography (to avoid foaming and spluttering at arc striking etc.). At the same time concentration of the trace elements and standardisation of the sample may be reached.

2. Earlier pretreatment for Co- and Mo-determinations

At first a pretreatment was applied as it is described in literature [2,12,13]. In short this pretreatment consists of: dry ashing of the sample (mostly 10 grams) for 12 hours at 450° C, *e.g.* in a muffle furnace — exclusion of silica inclusions by soda melt — dissolving the melt in dilute acid — precipitation of trace elements, iron and aluminium (added as a carrier) by supply of chemicals, *e.g.* oxyquinoline — filtration of the precipitate, followed by dry ashing. The sample consists then of Al_2O_3, Fe_2O_3 (some percents) and trace elements (mostly about 0.01%).

In this way, however, we could not succeed in obtaining spectrochemical analysis results, agreeing sufficiently with colorimetric ones for Co and Mo. In the mean the spectrochemical results were about 30% lower.

3. Application of wet ashing

This discrepancy disappeared (see IV. 4) when the first dry ashing and the soda melt were substituted by wet ashing with H_2SO_4, HNO_3, and later on with $HClO_4$. To avoid absorptions at $CaSO_4$, etc. the diluted destruction fluid is boiled for half an hour, whereupon the silica and the occasional calcium sulphate are filtered. The filter is washed two times with hot very diluted sulphuric acid. In the dilute acid filtrate the precipitate is obtained as described above.

The time required for a pretreatment is about the same in both cases (III. 2 and 3).

4. Pretreatment for Cu-determinations

When one is only interested in the copper content of the sample a dry ashing suffices for reason of the relatively high content in the original sample. After addition of K_2SO_4 as a spectroscopic buffer the sample is ready for spectrography [1,2,14].

The simultaneous determination of Cu in the presence of Co, Mo, etc. is in preparation.

IV. MEASUREMENTS

1. Internal standard

The large fluctuations in the intensity of spectral lines in an arc require application of an internal standard for an accurate deduction of contents in the sample from measured intensities. In orientating experiments concerning Co- and Mo-determinations the results were as follows. When no internal standard is applied and the required contents are deduced from the measured densities of the photographed spectral lines, the accidental error is five times larger than in the case of the application of an internal standard method as also described in this paper (*cf.* IV. 3); when the contents are deduced from line/background ratios the accidental error is a factor two or three larger.

As analysis lines we used Co 3453.5, Mo 3170.35 and Cu 3274.0 A. According to the literature[2] we first applied as reference lines Fe 3452.0, Fe 3197.0 and Ag 3280.7 A, resp.

Ag 3280.7 is a perfect standard line. The difference in upper level of both elements amounts to 0.1 eV (Cu 3.7, Ag 3.8 eV). This means that at an arc temperature of about 4000° K a temperature variation of 500° causes a variation of only 3½% in the relative intensity of these lines*.

Both the iron lines possess an upper level of about 6 eV, while that of the Co- and Mo-line is about 4 eV. Now at 4000° K a variation of 100° K gives a variation of 15% in relative intensities. A wavelength identification of about 80 iron lines on our plates in the region between 3500 and 3100 A showed that only one suitable iron line with an upper level of 4 eV is present, namely 3191.65 A. It may be used in combination with Mo 3170.35.

2. Proportionality between spectral relative intensity and content ratio in the sample

In a standard graph measured relative intensities are plotted against trace element content of the sample at fixed amounts of Fe in the sample. The varying Fe-content of the analysis samples — up to now colorimetrically determined[15] — may be taken in account *e.g.* with the help of an iron correction curve[1,2].

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* *Cf. e.g.* form. II. 3 in the first reference. As a consequence a stringent equality between standard and analysis sample is not required at all in such a case; *cf. loc.cit.* pages 118 and 125.

The procedure of relative intensity measurements includes important corrections for spectral background[1,2] and spectral inhomogeneity (*cf.* II.3)[1].

The amount of the element in question (*e.g.* Cu, Co), originating from electrodes and chemicals, must be often taken into account. These so-called blank amounts and the correlated relative intensities may be determined with the help of a graph in linear plotting, as it is illustrated in Fig. 2.

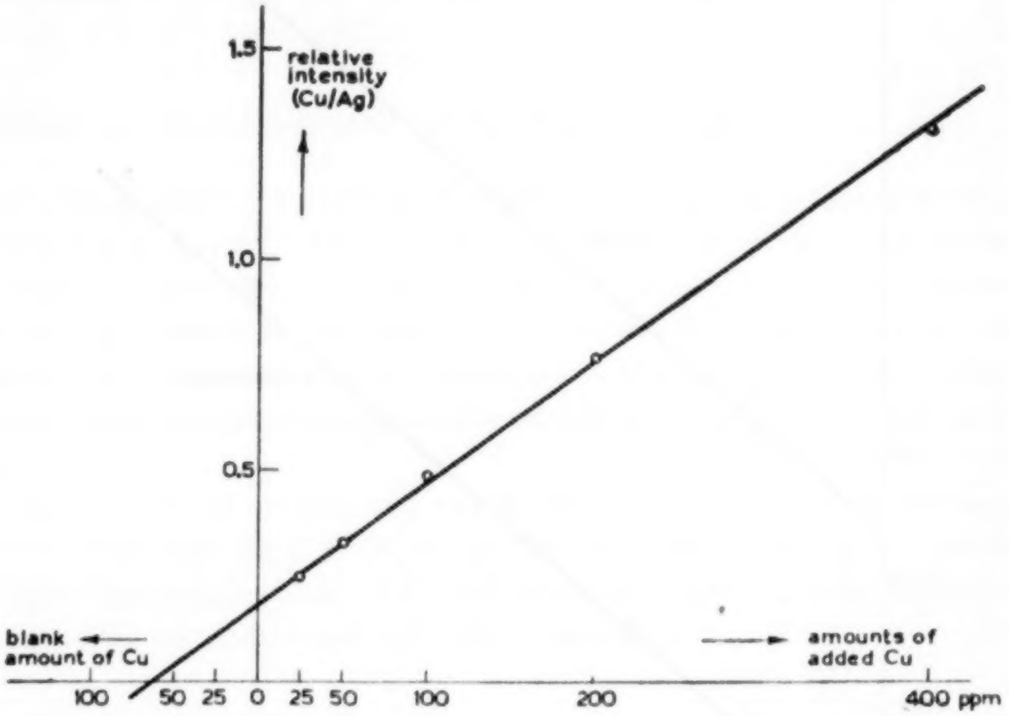

Fig 2

Fig. 2. Linear plotting of relative intensities against content to determine a blank amount of copper.

After application of the required corrections our standard graphs in double logarithmic plotting had approximatively a 45° slope. This means that in the content ranges considered (Co, Mo: 30—1000 ppm; Cu: 25—400 ppm; Fe some percents; Ag: 100—400 ppm) there is proportionality between relative intensities in the arc and content ratio in the sample.

This conclusion was confirmed by a "dilution test". To a sample consisting of Al_2O_3, 5% Fe_2O_3, 500 ppm Co and Mo Al_2O_3 have been added, the first time half the weight of the sample, the second time the full weight. In that way the trace element standard ratio had not been changed and indeed the measured relative intensities in spectra of the original and diluted samples agreed within the experimental margin*.

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* Quantitative results: pages 92 and 102 in first reference.

References p. 282.

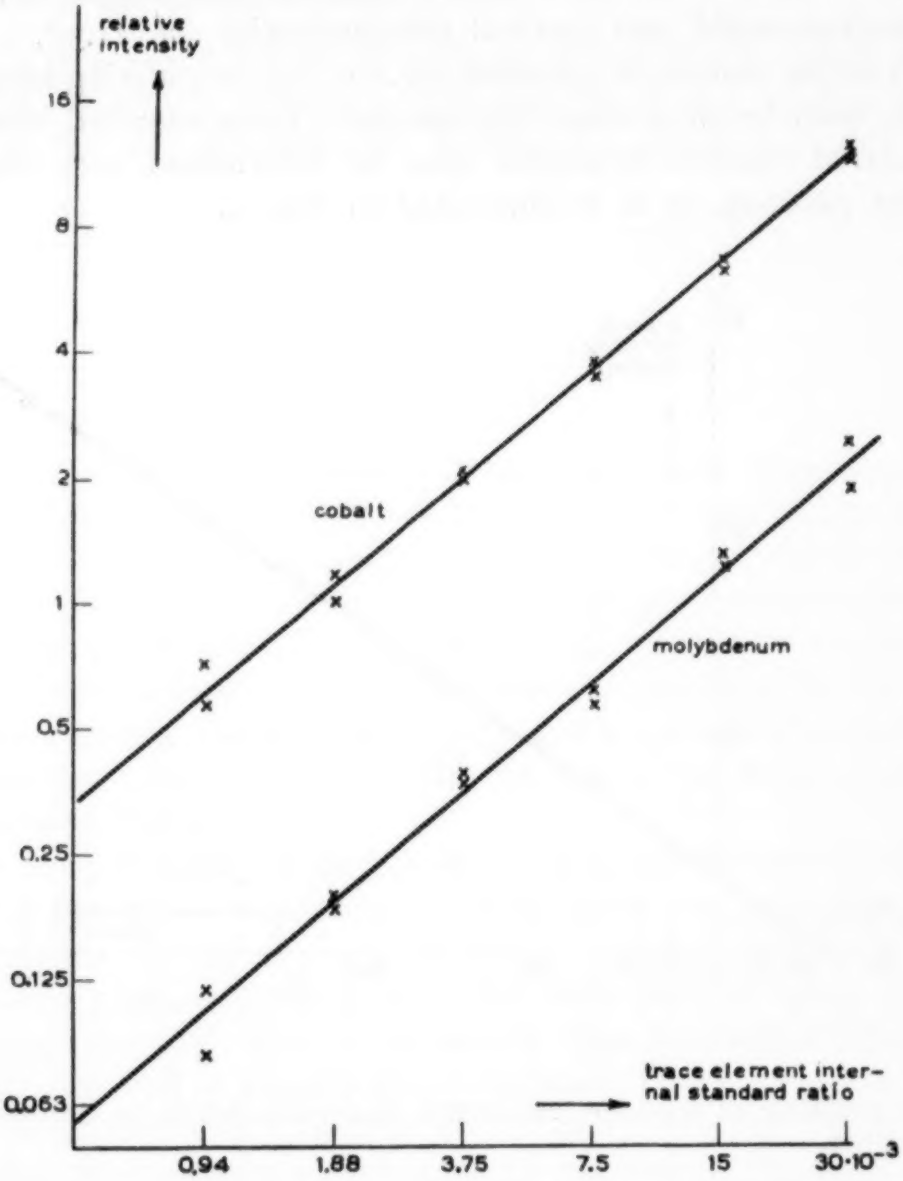

Fig. 3. Calibration curve by the help of which relative intensities can be converted into contents in the sample without application of an iron correction curve. On the abscissa the content ratio Co/Fe or Mo/Fe has been plotted; on the ordinate the line intensity ratio Co 3453.5/Fe 3452.0 or Mo 3170.35/Fe 3197.0.

Consequently for calibration one graph suffices, in which the intensity ratio is plotted against the content ratio of trace and reference element; see Fig. 3. An iron correction curve is superfluous.

3. Spectrographic and spectrochemical reproducibility

When we deal with "spectrography" only the physical part of the determination is meant, starting with electrode filling up to the determination of relative intensities. The term "spectrochemistry" is concerned with the complete analysis starting with plant ashing up to content determination, deduced from measured relative intensities via calibration.

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The spectrographic accuracy* of the relative intensity measurement in a single spectrum for the pairs of lines mentioned sub IV. 1 appeared to be 8%. This result is based on about 100 measurements.

The spectrochemical reproducibility* amounts to 10%. It is a result of amply 100 determinations.

These results are satisfactory for the analysis in question. For further details and a discussion of errors the first reference may be consulted.

4. Comparison of colorimetric and spectrochemical results

In a first experiment Cu has been determined in 50 grass samples in colorimetric and spectrochemical way. The mean of both series of determinations in dry material was 12.8 ppm (12.77) and 12.8 (12.84), resp. It may be concluded that there are no systematical deviations between both methods. The accidental deviations in the couples of results, obtained in the analysis of the same samples in both ways, were in agreement with the accidental error of 10% for each method separately.

After several series of orientating experiments also for Co and Mo comparable results have been obtained with a smaller number of samples. (10 samples; Co: 0.70 ppm spectrochemical, 0.61 colorimetric; Mo: 1.8 and 1.75, resp.).

The check will be continued for other elements, *e.g.* Zn.

ACKNOWLEDGEMENTS

The first author wishes to thank the National Council for Agricultural Research (T.N.O.), for their permission to publish this research in a thesis and in this paper. Gratitude goes also to all the people in the laboratory who contributed to the research with their interest, help and discussions, especially to Prof. Dr J. M. W. MILATZ, the director of the laboratory.

SUMMARY

This paper deals with the spectrochemical determination of some trace elements (Cu, Mo and Co), especially in plant samples. Data are given about the choice of light source and spectral apparatus, as well as detailed remarks concerning the optical arrangement.

In the concentrating pretreatment with precipitating chemicals a wet ashing has been proved to give better results than a dry ashing.

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* The standard deviation D is given. For a series of spectra belonging to one sample D is calculated according to the well-known formula: $D = \sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}}$ (x and $\bar{x}$: actual and mean value, n: number of measurements).

RÉSUMÉ

Cet article concerne l'analyse spectrochimique de traces de cuivre, molybdène et cobalt, en particulier dans les plantes. On traite du choix de la source lumineuse, de l'appareil spectral et de l'arrangement optique.

En ce qui concerne le traitement préalable de concentration, la minéralisation par voie humide est préférable à celle par voie sèche.

ZUSAMMENFASSUNG

Dieser Artikel behandelt die spektrochemische Bestimmung einiger Spurenelemente (Cu, Mo und Co), besonders in Pflanzenproben. Es werden sowohl Angaben gemacht über die Wahl der Lichtquelle und des Spektralapparates, als auch eingehende Bemerkungen, die die optische Anordnung betreffen.

Bei der Vorbehandlung mit Fällungsreagenzien zur Konzentration wurde bewiesen, dass eine Veraschung auf nassem Wege bessere Werte ergab als eine Veraschung auf trockenem Wege.

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QUALITATIVE ANALYSIS WITH A POLAROGRAPHIC OSCILLOSCOPE *

by

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Whilst the majority of authors[1] try to reach in oscillographic polarography a high degree of accuracy for quantitative determinations, it is the aim of the present author[2] to adapt the cathode ray oscilloscope so as to be useful for a rapid qualitative analysis. It will be shown that such an analysis is also quantitative to a certain degree.

The experimental arrangement is adapted so as to show on the oscilloscope the potential-time (V-t) curves, and this is achieved by the scheme of connection shown in Fig. 1. An alternating current, i, passes from a source A of large voltage E (120 to 220 volt) across a large variable resistance R (of the order of 100,000 ohms) through the electrolytic cell M with a polarizable dropping or streaming mercury electrode and an unpolarizable layer of mercury at the bottom of the cell filled with an electrolyte. As the polarization (or back e.m.f.), V, of the cell

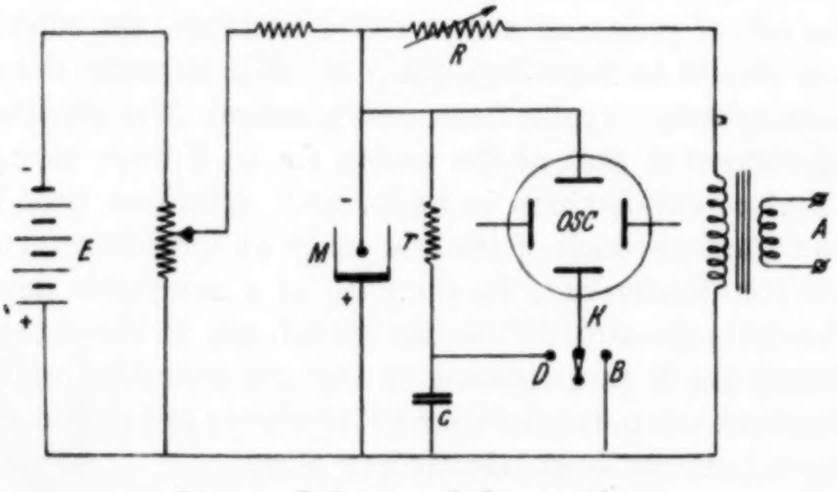

Fig. 1. Scheme of Connections.

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* Read at the Symposium on Analytical Chemistry held at the University of Birmingham, September 11-12, 1952.

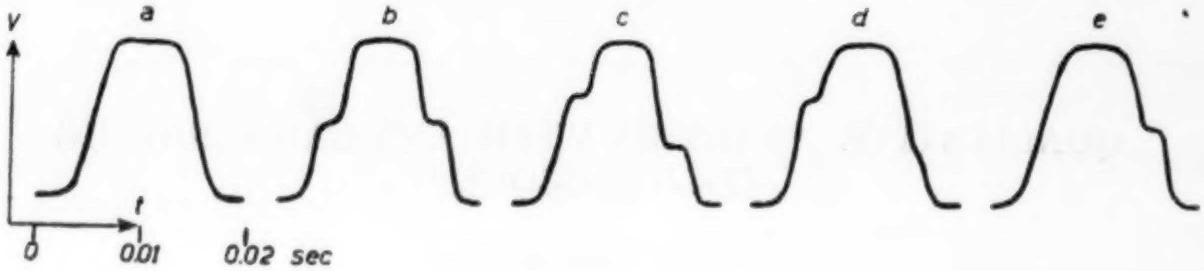

Fig. 2. Various types of *V-t* curves.

and its resistance are both negligibly small compared with E and R, the form of the sine-curve of the alternating current, $i = \frac{E \sin \omega t}{R}$ remains independent of the electrolytic processes within the cell. The value of i varies from 0.5 to 1 mA for the dropping electrode, and from 2 to 6 mA for the streaming electrode. The polarizable and unpolarizable mercury electrodes are connected to the horizontal plates of the cathode ray oscilloscope, the time-base showing the changes of the polarization V. In order to apply to the polarizable electrode negative potentials, a constant E.M.F. is also applied to the mercury electrodes, such that when the voltage acting on the cell varies during one half-period of the alternating current from —1 to +1 volt, the polarization V, *i.e.* the potential of the polarizable mercury electrode, varies between 0 to —2 V from the potential of the bottom mercury layer.

To avoid the fall of potential across the electrolyte, the concentration of the basic electrolyte should be kept high (*ca.* 1 to 2N). In most determinations the presence of atmospheric oxygen does not interfere. Usually the frequency of the alternating current is that of the mains, *i.e.* in Europe 50 c.p. sec.

In the presence of depolarizers in *ca.* 0.001N solutions time-lags appear on the cathodic and anodic branch of the *V-t* curve at the potential of the reduction or oxidation of the depolarizer. In the case of a reversible depolarization the time-lags at the cathodic and the anodic branch are at the same potential. The length of the time-lag is proportional to the concentration of the depolarizer. The various types of the potential-time (*V-t*) curves are shown in Fig. 2.

Curves are due a. to the basic electrolyte alone.
b. to the admixture of a reversible depolarizer, *e.g.* of Tl^+, Pb^{+2} or Cd^{+2} -ions.
c. to an irreversible depolarizer, *e.g.* of Zn^{+2} or Bi^{+3} -ions.
d. to an irreversible depolarizer, which gives a very indistinct time-lag at the anodic branch, like Fe^{+2}, Co^{+2}, Ni^{+2}, Mn^{+2}-ions.
e. to an irreversible depolarizer, which shows only an anodic time-lag, like Cu^{+2} or In^{+3} ions in H_2SO_4.

When we are dealing with the mixtures of depolarizers in the electrolyte the

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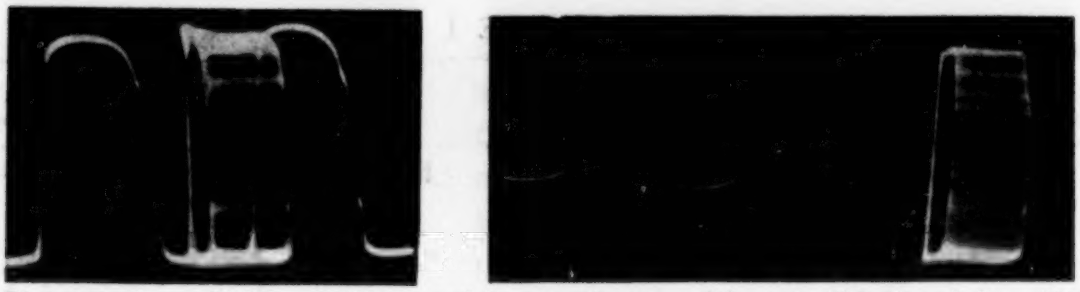

Fig. 3. ***V-t*** **curve and the oscillographic spectrum of brass dissolved in nitric acid (with dropping electrode).**
V-t curve and oscillographic spectrum of an ammoniacal solution containing cations Tl^+, Cd^{+2}, Zn^{+2}, Fe^{+2} and Mn^{+2} (with streaming electrode).

corresponding number of time-lags appear on the *V-t* curve. The current has to be increased accordingly by lowering the variable resistance *R* in order to charge the polarizable electrode to the most negative potentials as the electrolytic component becomes larger. However, the dropping of mercury causes shrinking of the oscilloscopic figure, which makes the determination of the time-lag potential difficult. A more stable figure is obtained when the time-base is accelerated from 50 c.p. sec. to some 100,000 so that each time-lag extends to a distinct line. The frequency of the time-base has to be so adjusted that it runs during one half-cycle only (*i.e.* during the cathodic or anodic branch), being zero during the other (Fig. 3). In this way "oscillographic spectra" are obtained, in which the characteristic potentials, almost coinciding with the polarographic half-wave potentials, denote the quality of the depolarizers. What is new in oscillographic polarography are the anodic time-lags, indicating the more or less irreversible processes, which furnish further characteristics of the quality. Thus zinc, which in acid solutions coincides cathodically with nickel, gives anodically a separate distinct line. Also the change of irreversibility to reversibility, effected through the addition of chlorides, may serve as a further specific indication for the ions Cu^{+2}, Bi^{+3}, Sb^{+3}, and In^{+3}. In the case of indium a distinct advantage over the polarographic test is presented, as the anodic line of In^{+3}, obtained in solutions of SO_4^{-2}, NO_3^-, ClO_4^- is more positive by 0.12 V than the line of cadmium, which coincides with indium in the polarographic half-wave potential (in chlorides). Because of this it is possible to determine oscillographically as little as 1% of indium in cadmium-containing zinc ores.

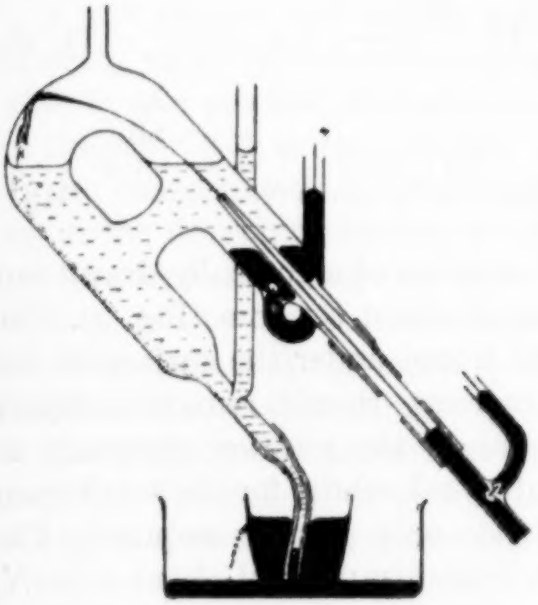

Fig. 4. The streaming electrode.

To eliminate entirely the shrinking of the *V-t* oscillograms, the streaming

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TABLE I

$1N$ HCl		
cathodic		anodic
H_2	1.6	H_2
Zn		
	1.4	
	1.2	Zn
As	1.0	
In, Cd	0.8	Cd
		In
Tl		Tl
Pb	0.6	Pb
Cu	0.4	Cu
Sb		Sb
Bi	0.2	Bi
Hg	0 V	Hg

$1N$ HNO_3 or H_2SO_4		
cathodic		anodic
H_2	1.8	H_2
Zn		
	1.6	
	1.4	Zn
	1.2	
Cd	1.0	Cd
Tl		Tl
Pb	0.8	Pb
Sb		In
	0.6	
Bi		
	0.4	Sb
		Cu
		Bi
Cl	0.2	
Hg	0 V	Hg

$1N$ NH_3, NH_4Cl		
cathodic		anodic
NH_4	1.8	NH_4
Mn		
Ge	1.6	
Fe		
Ni	1.4	
Zn		
	1.2	
	1.0	
		Zn
		Ga
Cd	0.8	Cd
	0.6	Ge
	0.4	
Cu		Cu
Tl	0.2	Tl
Cu		Cu
Hg	0 V	Hg

$1N$ KOH		
cathodic		anodic
K	1.8	K
Cr	1.6	
Zn	1.4	
Sb	1.2	
	1.0	
		Zn, In
	0.8	
Pb	0.6	Pb
Bi		
Tl	0.4	Tl, Bi
As	0.2	As
		Sb
Cu		Cu
Hg	0 V	Hg

mercury electrode has been introduced[3], which consists of a conically drawn out capillary, so that the inner diameter at the tip is about 0.1 mm (Fig. 4). The tip of the capillary should be placed about 5 to 6 mm under the surface of the electrolyte solution and the thin column of mercury should remain compact when streaming out of the solution. The volume of the solution necessary to fill the vessel of the streaming electrode is about 15 ml, whilst for the small open beaker used with the dropping mercury electrode only 1 ml is required. The depolarizers are clearly shown by this method in concentrations of about $0.001N$, and the indications disappear in $0.0001N$ solution. The potentials of cations, that give distinct time-lags are shown in Table I; other similar tables may be

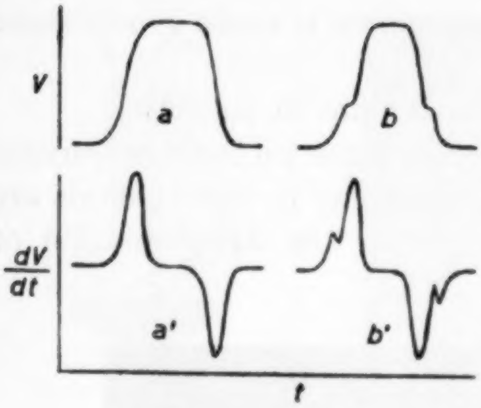

Fig. 5. Curves V-t and dV/dt-t of solutions a) without, b) with a depolarizer.

computed empirically when using other suitable basic electrolytes, *e.g.* cyanides, tartrates, citrates and oxalates. Also numerous organic depolarizers such as aldehydes, unsaturated compounds, nitro bodies, and quinones may be tabulated in this manner and determined.

However, the depolarizers may be shown more distinctly, and may even be quantitatively determined by plotting on the oscillographic screen the derivative dV/dt against the time, t, or potential V on the abscissa. This is effected by introducing into the scheme, parallel to the electrolytic mercury cell, a resistance of less than 1,000 ohms and a condenser of a capacity much smaller than that of the polarizable electrode (*ca.* 0.01 μF). Then the ordinate indicates a quantity proportional to the charging current ($i_c C'/C$), where C and C' are the capacities of the capillary electrode and the condenser in parallel, respectively. Each time-lag is in this way converted into a cut-in in the curve of the charging current. Since the sum of the charging current and the electrolytic current must remain constant $\dot{i}_c + \dot{i}_E = \dfrac{E \sin \omega t}{R}$ every decrease of the charging current means an increase of the electrolytic current in the opposite direction. The area of the cut-in represents the coulombs passed through the electrode, *i.e.* the amount of the electrolyzed depolarizer, which is proportional, like the diffusion current, to the concentration of the depolarizer.

A still simpler and a more stable figure is given by the function dV/dt-V, as it needs no synchronization and shows, by the depth of the cut-in, the quantity and, by the position of the peaks on the abscissa, the quality of the depolarizer, in the same way as the ordinary polarographic current-voltage curve. The values of the characteristic potentials are identical with those given in Table I. Here again the dropping mercury is suitable for inorganic analysis, whilst for organic analysis the streaming electrode is preferable, as it avoids complications of the figures due to consecutive and side-reactions, which take place at the slowly growing surface of the mercury drops. The method is of advantage where quick qualitative and approximate quantitative analysis of samples is concerned, *e.g.* in ore analysis, and particularly in organicanalys is for testing the purity of preparations. The following figures illustrate some examples:

Fig. 6 shows the presence of the cations Tl^+, Cd^{+2}, Zn^{+2}, Fe^{+2}, Mn^{+2} in an ammoniacal solution.

Fig. 7 shows manganese in iron ore; as here in the alkaline solution of triethanolamine the redox of Mn^{II}/Mn^{III} is considerably more positive

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than that of Fe^{II}/Fe^{III}, even a trace of manganese is made conspicuous in excess of iron.

Fig. 8 shows the presence of indium, lead and cadmium in zinc ore.

If the mercury used in the polarizable electrode contains metallic impurities (*e.g.* Cu, Bi, Sn, Pb, Tl, Cd, In, Zn) time-lags and kinks due to these metals are shown on the oscillographic curves. This may serve for the determination of impurities as well as for the determination of the depolarizers in solutions, if the metals in these solutions are electrolytically deposited in mercury and this is allowed to drop into an indifferent electrolyte. An advantage of this sort of analysis is that more base metals (*i.e.* of a more negative potential) can be determined in excess of the nobler metal, like traces of Zn or Cd in Pb, Sn, Tl, Cu, Hg, because the anodic dissolution of the nobler metals may be limited according to the direct voltage superposed on the alternating one. Admixtures of the order of 0.0001 to 0.001% in mercury are still traceable on the derivative curves.

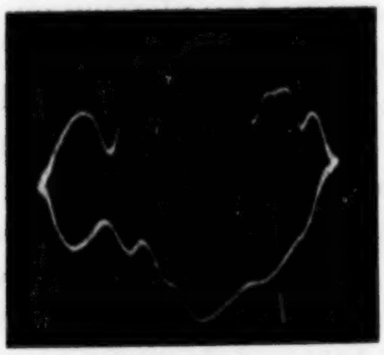

Fig. 6. Oscillogram dV/dt-V of an ammoniacal solution containing cations Tl^+, Cd^{+2}, Zn^{+2}, Fe^{+2} and Mn^{+2} (with streaming electrode).

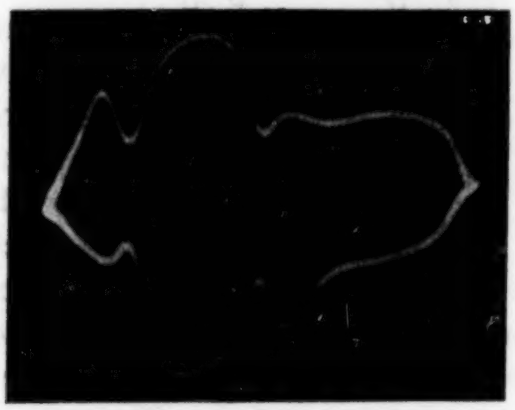

Fig. 7. Oscillogram of 1 *N* KOH, 0.25 *M* triethanolamine showing the presence of Mn and Fe (with dropping electrode).

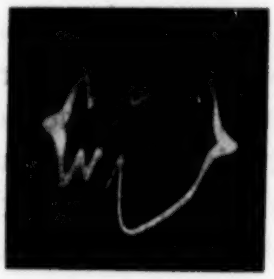

Fig. 8. Oscillogram of 1*N* KOH, 1*N* KCN of a concentrated solution of zinc containing Pb, In and Cd as impurities (with dropping electrode) shown by the three anodic maxima.

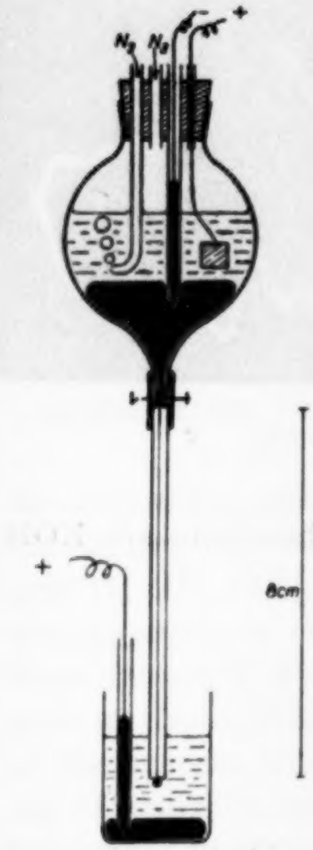

Fig. 9. Apparatus for the preparation of amalgams.

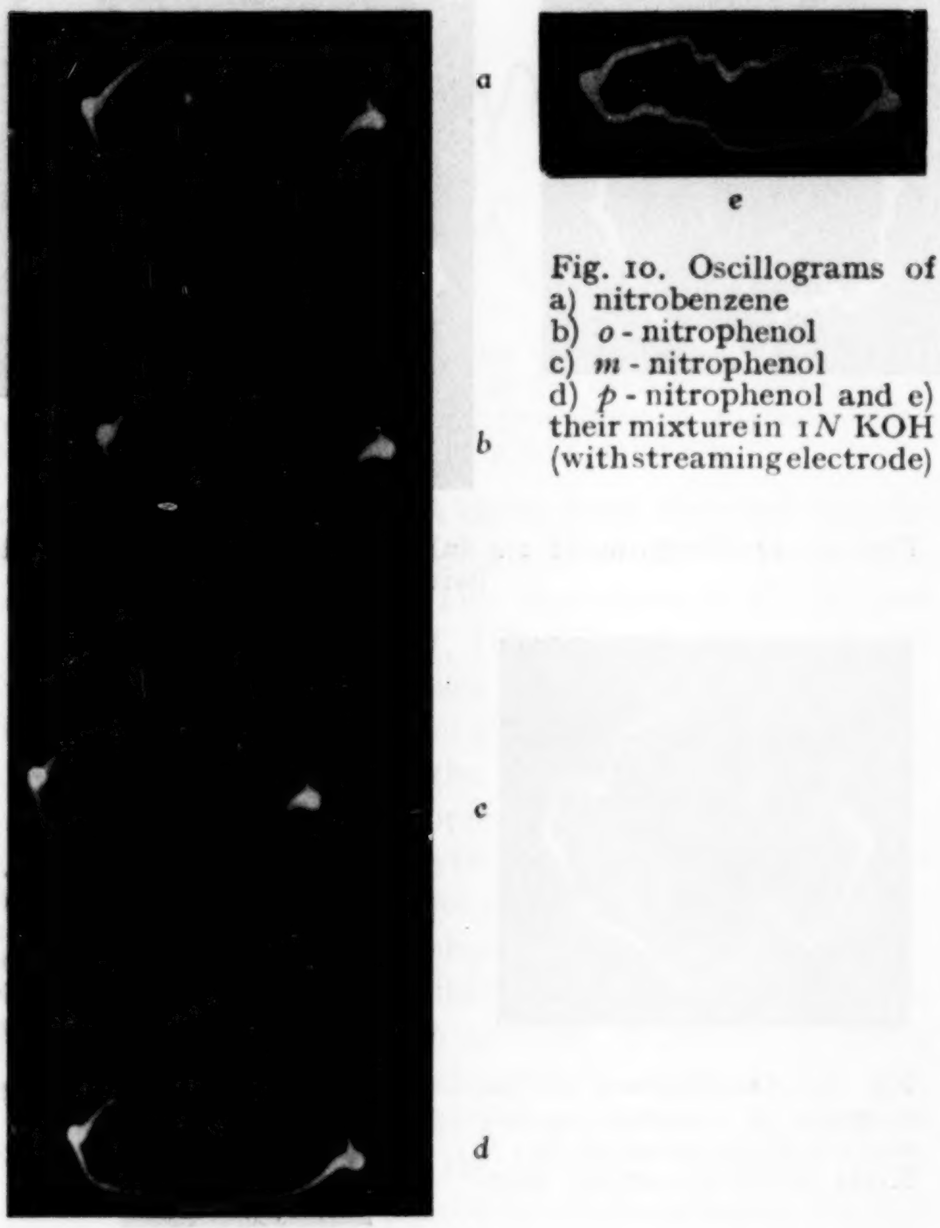

Fig. 10. Oscillograms of
a) nitrobenzene
b) *o* - nitrophenol
c) *m* - nitrophenol
d) *p* - nitrophenol and e) their mixture in 1*N* KOH (with streaming electrode)

The dropping electrode used for amalgams should have a wide inner diameter (0.1 mm) and be some 8 cm long, to let mercury pass quickly; the mercury reservoir need not be more than 12 to 15 cm above the tip of the capillary (Fig. 9).

In organic analysis the purity of isomers of depolarizers may be tested oscillographically and analysis of their mixtures is made possible. Figs. 10 show the dV/dt-V oscillograms of the three single isomers *o*-, *m*- and *p*-nitrophenols as well as that of nitrobenzene and of their mixtures. Each component is discernible by the respective potential of the peak at the abscissa. Fig. 11 shows the oscillograms of the three isomers of dinitrophenols 2:4, 2:5, 2:6 and Fig. 12 their mixture in 1*N* KOH. Similar cases of the oscillographic resolution of nicotinic, *iso*nicotinic and picolinic acids, further of isomers of aromatic nitro-aldehydes and of the nitranilines have also been obtained.

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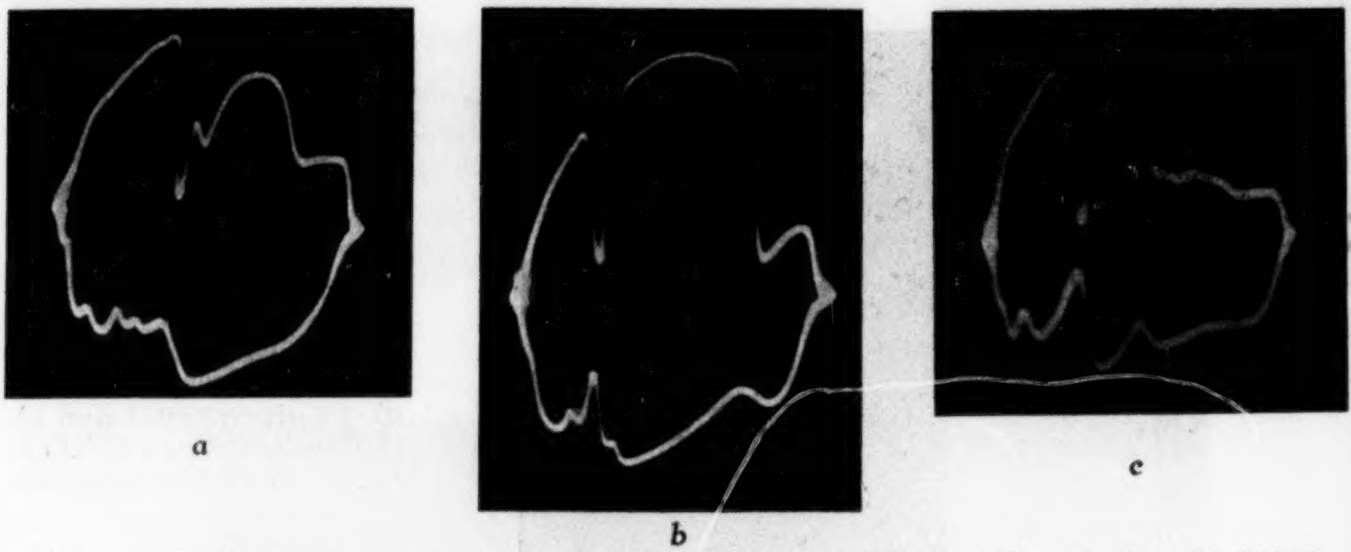

Fig. 11. Oscillogram of 2:4 (a), 2:5 (b) and 2:6 (c) dinitrophenols in 1*N* KOH (with streaming electrode).

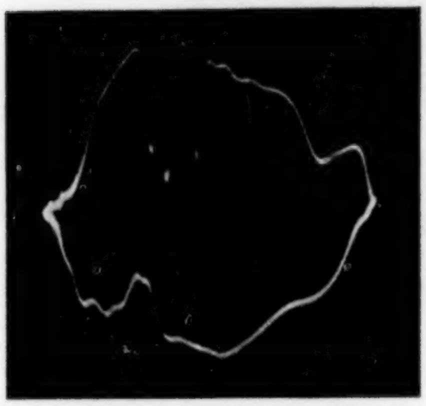

Fig. 12. Oscillogram of the mixture of isomers 2-4, 2-5 and 2-6 dinitrophenols in 1*N* KOH (with streaming electrode).

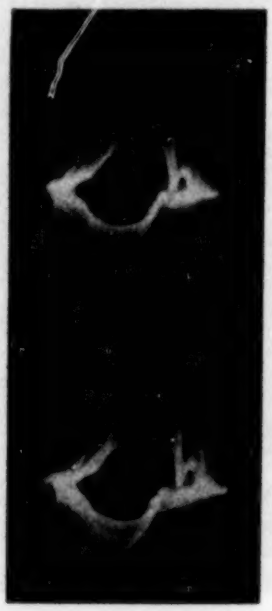

Fig. 13. Oscillogram of a pure sample of penicillin G (Roztoky, CSR); 3.5 mg in 1 ml of 1*N* Li_2SO_4, 0.01*N* H_2SO_4 at 0° C (with dropping electrode) the first minute after dissolution (Fig. below) and after three minutes (above).
Note the small cavity at the top of the cathodic branch.

A case where oscillographic analysis gives considerably more information than the polarographic one is that of penicillin. A fresh aqueous solution of penicillin when kept at 0° C in an acid solution of pH around 2 gives, in the first minutes, no effect. However, two waves appear after a certain time, which at first increase and later on decrease until they disappear entirely. The depolarizer, which is formed in the acidic solution and soon decomposes again, has been shown to be penicillenic acid, the unstable isomer of penicillin. In its turn it yields dimethylcystein and penillo-aldehyde, which are not shown polarographically in the solution of pH around 2. If these changes of a 0.01*M* solution of purest penicillin G in 1*N* Li_2SO_4 with 0.01*N* H_2SO_4 at 0° C are followed on the oscillogram dV/dt-V with the dropping or with the streaming mercury electrode, there appears, in the first few minutes, only a capacity effect due to adsorption of penicillin (Fig. 13). However, after some minutes several kinks gradually appear showing the

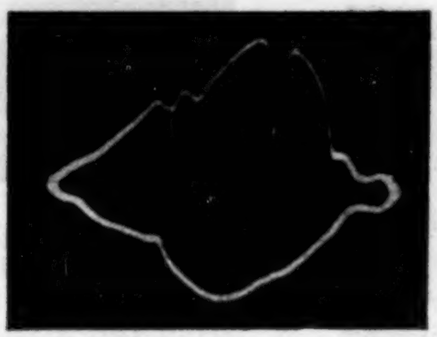

Fig. 14. Oscillogram due to an advanced decomposition of a penicillin sample at pH = 2 (with streaming electrode).

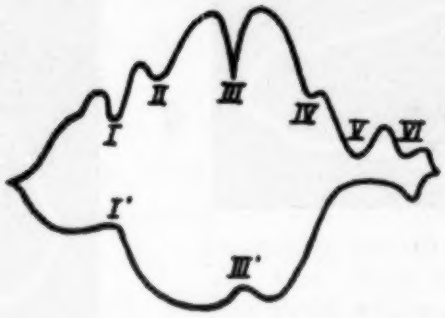

Fig. 15. The kinks on the dV/dt-V curve due to the decomposition products of penicillin in a weakly acidic solution.

decomposition products of penicillin, (Fig. 14). A closer study revealed that the cuts-in are due — as denoted in Fig. 15 — to dimethylcystein (I, I′), penicillenic acid (II, III, III′), catalysis by the —SH group (IV), deposition of H^+ (V) and penillo-aldehyde (VI). After some hours kinks II, III, III′ and IV vanish and there remain I, I′, markedly deepened. Decomposed samples of penicillin show, even at the very beginning of decomposition, kinks (especially I and III) already at the instant when the sample is dissolved in the ice-cold solution. Only 3.5 mg of penicillin are necessary for 1 ml, if the dropping electrode be used, or 50 mg for the streaming electrode vessel. The electrolytic vessel has to be surrounded by ice; the presence of air has no influence on the shape of the curves.

There are several noxious depolarizers contaminating the atmosphere in industrial works, which may be checked oscillographically, *e.g.* carbon disulphide, hydrogen sulphide and sulphur dioxide. For such analyses, either the dropping mercury electrode is advisable, in a small vessel specially adapted (Fig. 16), through which air is drawn by a small electrically driven turbine, or a smaller size vessel with the streaming electrode. After air has been passed for several minutes through the most suitable electrolyte, the dV/dt-V diagrams show the characteristic curve with more or less developed kinks, according to the amount of the noxious vapour in the atmosphere.

For carbon disulphide the best electrolyte is $2N$ sodium acetate with $2N$ acetic acid, in which traces of carbon disulphide give cathodic and anodic kinks at about -0.9 V (Fig. 17). This reaction shows high sensitivity, revealing

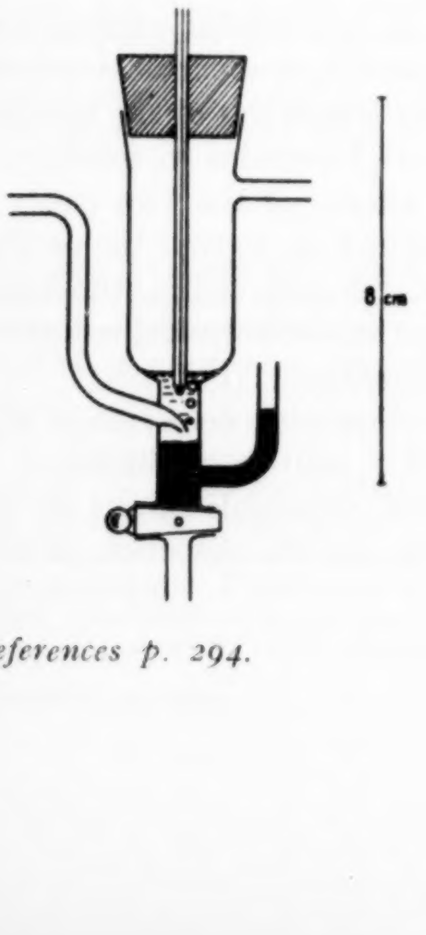

Fig. 16. An electrolytic vessel for the analysis of the atmosphere.

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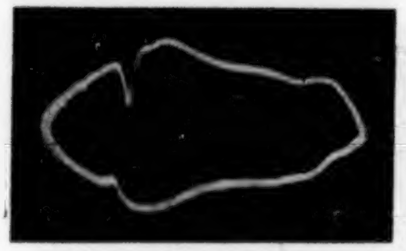

Fig. 17. Oscillogram of $2N$ acetic acid and $2N$ sodium acetate after the absorption of CS_2 from the atmosphere (with dropping mercury electrode).

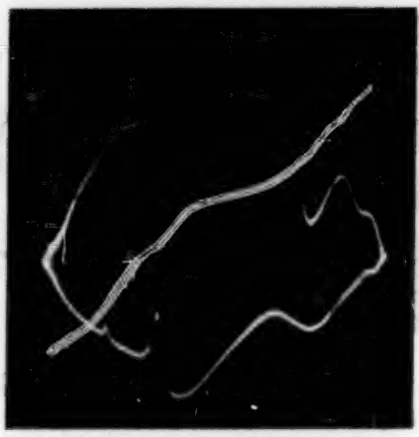

Fig. 18. Oscillogram of $2N$ acetic acid and $2N$ sodium acetate after the absorption of CS_2 from the atmosphere (with streaming mercury).

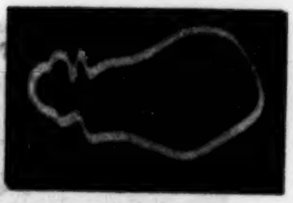

Fig. 19. Oscillogram of $2N$ H_2SO_4 after the absorption of SO_2 from the atmosphere (with dropping mercury).

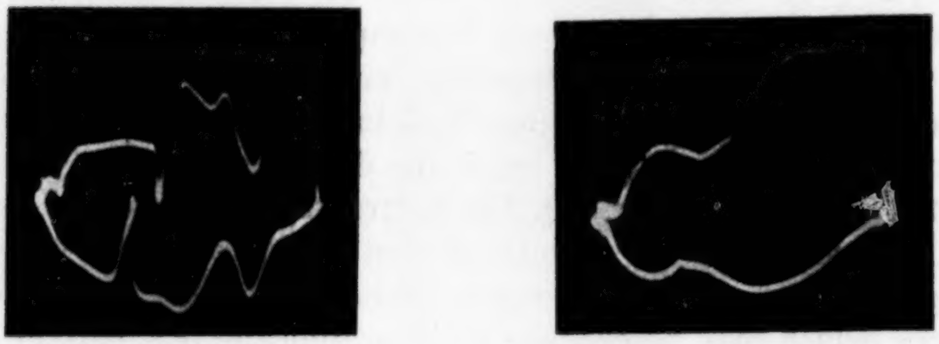

Fig. 20. Oscillogram of: a) a solution of $1N$ LiCl, $0.1N$ $FeSO_4$ in the presence of atmospheric oxygen.
b) in the atmosphere of nitrogen (with dropping mercury electrode).

1 μg per ml of CS_2 in the solution. Hydrogen sulphide gives a similar oscillogram; however, the two compounds can be distinguished, as CS_2 is much less soluble in the electrolyte than H_2S and is, consequently, easily driven out of the solution by passing nitrogen or pure air through it, whereas H_2S remains in solution.

A still more conspicuous difference between the effects of the two gases is shown when the direct component of the voltage is turned on, so that the oscillogram does not reach the negative potentials. Then in the case of CS_2, the kinks disappear, whilst with H_2S they remain, (this is due to the electrolytical reduction of CS_2 to H_2S, which takes place only at negative potentials). (Fig. 18).

However, the most sensitive electrolyte for the oscillographic detection of H_2S is $1N$ NH_4Cl, $1N$ NH_3, and this shows the kinks of CS_2 only very slightly.

The presence of sulphur dioxide produces marked reversible kinks in $2N$ H_2SO_4 and this electrolyte is, therefore, very suitable for the detection of SO_2 in the atmosphere. (Fig. 19).

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The presence of hydrocyanic acid in the atmosphere is best shown by bubbling air through an acetate buffer solution or 1*N* LiOH. Kinks appear at positive potentials of the cathodic branch.

Atmospheric oxygen, as has been pointed out above, is almost without effect in oscillography, since its electro-reduction proceeds usually slowly. However, there are catalysts like Mn^{+2}, Fe^{+2} in neutral solutions of alkali chlorides, which by their presence cause a sharp cathodic and anodic cut-in into the dV/dt-V or dV/dt-t curve (Fig. 20) when the dropping mercury electrode is used, and if oxygen is present. The height of these peaks depends on the oxygen pressure and shows even the slightest traces of oxygen, especially when the alternating current is increased to more than 1 mA. A suitable solution to be used for the oscillographic oxygen test is 0.1*N* $MnCl_2$ in 1*N* LiCl.

The oscillograms may be photographed on films and the characteristic details measured on enlarged copies.

To facilitate research in oscillographic polarography and to furnish a simple tool for routine analysis, the National Enterprise Křižík-150, Prague, has constructed a portable unit called "Electronic Polaroscope", containing a cathode ray tube and equipment which yields directly the most suitable function dV/dt-V, by connecting to it the mercury cell on one side and the mains on the other.

SUMMARY

The cathode ray oscilloscope has been adapted for rapid qualitative analysis with the dropping or streaming mercury electrode. Provision is made so that the oscilloscope shows the potential-time curves as well as the derivative-potential curves.

The potentials of cations which give distinct time-lags have been computed. Numerous organic depolarizers such as aldehydes, unsaturated compounds, nitrocompounds and quinones may be similarly determined.

The method is of advantage where quick qualitative and approximative quantitative analysis of samples is concerned, *e.g.* in ore analysis, or especially in organic analysis for testing the purity of preparations and distinguishing isomers.

Decomposition of fresh aqueous solutions of penicillin may be followed by this method of oscillographic analysis. In addition, there are several other applications of the method, *e.g.* rapid qualitative analysis of carbon disulphide, hydrogen sulphide, hydrocyanic acid and sulphur dioxide in the atmosphere of industrial works.

RÉSUMÉ

L'auteur propose une application de l'oscilloscope à rayon cathodique à l'analyse qualitative rapide. L'oscilloscope montre des courbes potentiel-temps et des courbes dérivée du potentiel-temps de l'électrode à goutte ou à courant de mercure. Les potentiels des cations donnant des paliers distincts sont calculés, de même que ceux de nombreux dépolarisants organiques, tels que les aldéhydes, les composés non saturés, les nitrocomposés et les quinones. La méthode proposée s'adapte bien aux analyses qualitatives rapides et aux analyses quantitatives approximatives; exemples: analyses de minerais, ou spécialement analyse organique pour le contrôle de la pureté des préparations et pour la distinction d'isomères. La décomposition des solutions aqueuses de pénicilline peut être suivie par cette méthode d'analyse oscillographique. D'autre part, il existe beaucoup d'autres applications, par exemple: analyse qualitative rapide du sulfure de carbone, de l'hydrogène sulfuré, de l'acide cyanhydrique et de l'anhydride sulfureux dans l'atmosphère.

ZUSAMMENFASSUNG

Das Kathodenstrahloszilloskop wurde für rasche qualitative Analysen verwendet. Das Oszilloskop zeigt Potential-Zeitkurven und Ableitungspotentialkurven der tropfenden oder strömenden Quecksilberelektrode.

Die Potentiale der Kationen, welche bestimmte Zeitverschiebungen geben, werden errechnet. Zahlreiche organische Depolarisatoren, wie Aldehyde, ungesättigte Verbindungen, Nitroverbindungen und Chinone können ähnlich bestimmt werden.

Die Methode ist von Vorteil bei schnellen qualitativen und ungefähren quantitativen Analysen von Proben, z.B. für Metallanalysen oder besonders für organische Analysen zur Prüfung auf Reinheit der Präparate und Unterscheidung von Isomeren.

Die Zersetzung von frischen wässrigen Lösungen von Penicillin kann mit der oszillographischen Analysenmethode verfolgt werden. Zusätzlich bestehen noch mehrere andere Anwendungen dieser Methode, z.B. die schnelle qualitative Analyse von Schwefelkohlenstoff, Schwefelwasserstoff, Cyanwasserstoff und Schwefeldioxyd in der Atmosphäre von Industrie-betrieben.

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BOOK REVIEWS

The Principles of Line Illustration, by L. N. STANILAND, A.R.C.S., D.I.C., A.R.W.A., Burke Publishing Company Ltd., London, 1952. xii and 212 pages, 166 illustrations, 25*s* net.

On the shelves of the scientist, this book is a strange bird, but how welcome it must be to those who are struggling with the problem of producing suitable line illustrations for their publications ! Few people would be better qualified to write a book like this one than its present author who is a biologist as well as an artist and who, in addition, has the gift of a clear and straightforward style of writing.

In five chapters (Techniques in line drawing; Aids to accurate drawing; The use of colour; Graphs, diagrams and maps; Some help with lettering) and an Appendix (Hints and tips) the subject matter is clearly set out, helping students and research workers to overcome the difficulties met with when making line drawings, either for their own use or for reproduction.

The present reviewer happens to know from almost daily experience how very divergent the quality of illustrations submitted with scientific manuscripts can be. To some authors of books and—honestly speaking—of papers for these *Acta*, he would like to say: let STANILAND be your guide for future illustrative material. The book is full of valuable hints, and, although the professional draughtsman may have different views on some details, it will excellently serve its purpose of indicating the traps for the unwary.

One hint might have usefully been added: when sending the finished drawings to the editor together with the manuscript of book or paper, don't stick the drawings in the manuscript, and don't write the legends directly underneath the drawing, but list them separately; the drawing and its legend have to go a different way, the former to the blockmaker, the latter to the printer.

The book is very beautifully produced, paper, printing, binding, jacket, all are exemplary. Small wonder that the same can be said of the numerous line illustrations.

W. GAADE (Amsterdam)

Die silicatische Tonminerale von DR. K. JASMUND. No. 60 der Serie Monographien zu Angewandte Chemie und Chemie-Ingenieur-Technik. Verlag Chemie, G.m.b.H. Weinheim-Bergstrasse. 142 Seiten, 40 Abb. und 67 Tabellen. 1951.

De cette monographie qui compte 142 pages, la plus grande partie (p. 33-142) est consacrée à la description détaillée des différents minéraux siliceux (argiles), leur composition chimique, leurs propriétés physiques et structures moléculaires (par rayons X, microphotographies électroniques, etc.).

Cet ouvrage, accompagné d'un grand nombre de tables et de données numériques, est excellent et très utile à tous ceux qui s'occupent de cette matière. Etant donné qu'il existe des différences d'opinion sur quelques structures, il va sans dire que le livre porte le cachet de l'opinion personnelle de l'auteur. Cependant celui-ci a quand même donné un exposé impartial des différents points de vue. Bref, ce livre nous présente une étude critique que chaque spécialiste dans ce domaine appréciera.

Par contre, l'importance des 25 premières pages du livre nous semble assez douteuse. L'auteur présente un exposé — par la force des choses très superficiel — de la genèse, des méthodes de recherche, de la synthèse et de quelques propriétés importantes pour l'emploi industriel des argiles. A notre avis, ceux qui profiteront du reste du livre n'auront pas besoin de cette introduction, et pour ceux qui ne sont pas encore orientés, elle est beaucoup trop superficielle.

A la fin de l'ouvrage se trouve une bibliographie assez complète qui doit être très utile aux spécialistes. La littérature dans ce domaine se trouvant dans des revues bien divergentes: chimiques, physiques, agronomiques et céramiques; cette bibliographie, soigneusement préparée, sera la bienvenue.

C. J. van Nieuwenburg (Delft)

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL RESULTS

Biological Methods Group

The Eighth Annual General Meeting of the Biological Methods Group of the Society of Public Analysts and Other Analytical Chemists was held in the Chemical Society's Rooms, Burlington House, London W.1, on Thursday, December 11th, 1952, at 6.15 p.m. Dr. Collier, Chairman of the Group, was unavoidably delayed and his place was taken by Mr. A. L. Bacharach.

The following were elected Officers of the Group for the ensuing year:

Chairman — Dr. H. O. J. Collier
Vice-Chairman — Dr. L. J. Harris, F.R.I.C.
Hon. Secretary & Treasurer — Mr. S. A. Price, B. Sc., Walton Oaks Experimental Station, Vitamins Ltd., Dorking Road, Tadworth, Surrey.

The Annual General Meeting was followed at 6.30 p.m. by an Ordinary Meeting of the Group, at which Dr. H. O. J. Collier was in the Chair and thirty-two other members and guests were present. The following papers were presented and discussed:

A Method of Identifying the Presence or Absence of Splenin "A" and Splenin "B" in Serum using Guinea Pigs, by Raymond Greene and Josephine Vaughan-Morgan.

The variation of bleeding time in guinea pigs living under controlled conditions was established. Injections were made of the chloroform-soluble Splenin "A" of normal serum and the acetone-soluble Splenin "B" from the serum of patients with rheumatoid arthritis, and the effect on the normal bleeding time noted.

A description of the method was given, followed by a discussion of the difficulties encountered and the reasons for carrying out the investigation.

The Application of Large Plate Methods to Microbiological Assays of Antibiotics and Vitamin Products, by K. A. Lees and J. P. R. Toothill.

Part I. *Precision Assays.* By careful control of conditions, and by development of suitable 12 × 12 designs, several unknowns can be simultaneously assayed on a single large plate with an error of about 1%. This technique has been developed for assaying purified antibiotic and vitamin products when the error due to impurities in the sample is known to be less than 1%. A feature of this assay method is that, besides the usual checks on validity, such as for parallelism and curvature, direct checks on the accuracy of the dilutions employed are available from the internal evidence of each 12 × 12 design.

Part II. *Routine Assays.* To obtain assays with an error of about 5% by large plate methods suitable for routine purposes, some of the checks on accuracy and validity in the 12 × 12 designs have been eliminated, thus enabling 8 or 9 preparations to be compared on a single plate.

For the routine designs dealing with 8 preparations, some simple arithmetic and a nomographic evaluation of the potency ratios enable the best estimates of these ratios to be objectively obtained. Replicate assays were examined for consistency (using the error of the assay method as determined over long periods) by means of a simple rough test.

FÜR EINE KORREKTE DARSTELLUNG DER pH-LEHRE

von

F. L. HAHN

Niza 64, México 6, D.F. (México)

I

Die folgenden Ausführungen werden dem Kenner der Materie stofflich kaum etwas Neues bringen, denn jedes Lehrbuch der Analytischen Chemie erwähnt, dass in wässrigen Lösungen nicht H^+-Ionen (freie Protonen) sondern H_3O^+-Ionen existieren, und ebenso werden einige weitere Änderungen der Theorie von Säuren und Basen als zwingend anerkannt; für praktische Zwecke aber werden diese Anschauungen mit dem Bemerken abgetan, dass man die Darstellung nicht durch sie zu komplizieren brauche, weil sie nichts an den quantitativen Beziehungen änderten. Neu und beachtenswert erscheint mir daher der hier zu erbringende Nachweis, dass alle Entwicklungen im Gegenteil wesentlich vereinfacht werden, wenn man sie von Anfang an und durchweg auf die jetzt als korrekt erkannten Beziehungen gründet.

Die klassische Lehre nahm an, dass Säuren und Basen im Wasser dissoziieren, also analoge Veränderungen erleiden; da aber die Säuren H^+- und die Basen OH^--Ionen bilden, erhalten wir zwei verschiedene Klassen von Dissoziationskonstanten und zwei Formeln zur Berechnung von pH-Werten. Dasselbe gilt für die Spaltung der Salze schwacher Säuren und Basen durch das Wasser (Hydrolyse), für die mittleren Salze von mehrwertiger Säuren einerseits und Basen anderseits, für Puffermischungen aus Säure und Salz oder Base und Salz, und schliesslich noch eine Formel für das Salz aus einer schwachen Säure mit einer schwachen Base (auch auf Ampholyte anwendbar), im ganzen also neun Formeln zur Berechnung von pH-Werten; davon bleiben bei sachgemässer Darstellung nur vier übrig, und diese sind klarer und einprägsamer als die bisherigen.

Die alte Formulierung der „Dissoziation" einer Säure

$$AH \rightleftarrows A^- + H^+ \tag{1}$$

ist unzutreffend; sie muss als Hydrolyse des Säuremoleküls oder, was auf das gleiche herauskommt, als Protonenabgabe des gelösten Stoffes an Wasser gedeutet werden, und damit rückt sie sofort in Parallele zu dem Vorgang, der bisher „Hydrolyse eines Basenkations" genannt wurde.

Literatur S. 309.

$$(2)\qquad AH + H_2O \rightleftharpoons A^- + H_3O^+$$

$$(3)\qquad BH^+ + H_2O \rightleftharpoons B + H_3O^+$$

$$(4)\quad \text{allgemein:}\qquad XH^{n+} + H_2O \rightleftharpoons X^{(n-1)+} + H_3O^+$$

Noch tatsachenwidriger wurde die Dissoziation der Basen und die Hydrolyse der Anionen formuliert, denn Moleküle BOH, die partiell in B^+ und OH^- dissoziieren gibt es gar nicht; Lösungen von Ammoniak in Wasser sind nicht deshalb schwächer basisch als gleich konzentrierte Natronlaugen, weil NH_4OH nur wenig dissoziiert ist, sondern weil es sich nicht bildet; und von einem Anion A^- kann durch Wasser nichts abgespalten werden (Hydrolyse = Spaltung durch Wasser), es kann also nicht hydrolysieren*. Die basische Reaktion entsteht in beiden Fällen nach

$$(5)\qquad B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$(6)\qquad A^- + H_2O \rightleftharpoons AH + OH^-$$

$$(7)\quad \text{allgemein:}\qquad Y^{i+} + H_2O \rightleftharpoons YH^{(i-1)+} + OH^-$$

Ziehen wir weiter in betracht, dass wir eine Erhöhung der Konzentration an OH^- durch die entsprechende Verminderung an H_3O geben müssen, unser pH-Skala entsprechend, dann ist Gl. 7. durch

$$(7a)\qquad Y^{(n-1)+} + H_3O^+ = YH^{n+} + H_2O$$

zu ersetzen, das ist aber nichts anderes, als Gl. 4 von rechts nach links gelesen. An allen vier Gleichgewichten, die bisher als Dissoziationen von Säuren oder Basen und Hydrolysen von Kationen oder Anionen gedeutet und durch vier verschiedene Konstantenarten beschrieben wurden, sind Wassermoleküle und Hydronium-Ionen** in durchaus analoger Weise beteiligt, und berücksichtigen wir das, so können wir mit einer einzigen Konstantenart: der Gleichgewichtskonstante in Acidoid/Basoid-Systemen auskommen. Statt der Vielheit aber der möglichen gelösten Substanzen: Säuren und Basen, gesättigte und mittlere Salze von Säuren und Basen, Salze zwischen schwachen Säuren und schwachen Basen (und Ampholyte), erhalten wir nur drei Klassen von reinen Stoffen, die gelöst sein können: Acidoide, Basoide und Ampholyte, also nur drei Formeln zur Berechnung von pH-Werten für reine Stoffe, und eine vierte für Puffermischungen.

Diese beträchtliche Vereinfachung wird nur möglich, wenn wir uns auf eine eindeutige Bezeichnungsweise für die verschiedenen Klassen von Stoffen einigen, und eine solche Bezeichnung, die eben bereits angedeutet wurde, muss demnach begründet werden.

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* „Hydrolyse der Anionen schwacher Säuren" ist ein Überbleibsel aus der Zeit, da man sagte: „Natriumacetat wird durch Wasser in Essigsäure und Natronlauge gespalten, und da diese stark, die Säure aber schwach ist, reagiert die Lösung alkalisch."

** Über Hydronium, Oxhydril und W als Zeichen für das Ionenprodukt des Wassers vgl. 6. Zu Acidoid, Basoid und Ampholyt, vgl. 4.

II

Wenn bisher die ausserordentliche Einfachheit der neueren und korrekten Behandlung der pH-Lehre nicht erkannt oder sogar bestritten wurde, so liegt das offensichtlich an einer sprachlichen Schwierigkeit: Essigsäure ist ein isolierbarer Stoff, den wir in reinem Zustand in eine Reagensflasche füllen können, und Ammoniumionen sind das nicht; wir sträuben uns also mit Recht dagegen, das Ammoniumion schlechthin eine Säure zu nennen, und müssen daher von „Säuren im engeren, klassischen Sinne" und „Säuren im erweiterten Sinne, nach BRÖNSTED"[1] sprechen oder von „Lewis-Säuren" usw.; das ist aber in längeren Ausführungen nicht möglich. Ich möchte vorschlagen, die Bezeichnungen Säure, Base und Salz als kennzeichnend für die formelmässige Zusammensetzung der chemischen Stoffe ungeändert zu verwenden, dagegen, wo es sich um die funktionelle Wirkung handelt von Acidoiden und Basoiden zu sprechen, ohne Rücksicht auf Molekül oder Ion: Acidoid ist in einem bestimmten System die Partikel, die Protonen abgibt, und Basoid die Partikel, die Protonen aufnimmt. Auch in den Redox-Systemen, zu denen die Acidoid/Basoid-Systeme nun in enge Analogie rücken, unterscheiden wir nicht nach dem Ladungszustand der Partikeln: die Elektronenspender, das Kation Fe^{+2} und das Anion I^-, sind den Elektronenbindern gegenüber Reduktoren, gleichgültig ob es sich bei diesen letzten um Moleküle Cl_2 oder Ionen Ce^{+4} handelt. In Redox-Systemen werden Elektronen ausgetauscht, und in Basacid-Systemen (wenn ich es wagen darf, diesen Ausdruck vorzuschlagen) Protonen.

Ebenfalls in völliger Analogie zu den Redoxsystemen erhalten wir nun eine einzige, allgemeine Formel für die Basacid-Systeme, die alle Einzelfälle deckt:

$$\underset{A_1}{XH^{n+}} + \underset{B_2}{Y^{i+}} \rightleftharpoons \underset{B_1}{X^{(n-1)+}} + \underset{A_2}{YH^{(i+1)+}} \tag{8}$$

Unabhängig von dem Zahlenwert der Koeffizienten n und i, die positiv, null oder negativ sein können, formen die Stoffe A_1 und B_1 wie A_2 und B_2 je ein Acidoid/Basoid-Paar, und die beiden Paare sind miteinander im Gleichgewicht (selbstverständlich können auch drei oder mehr Paare am Gleichgewicht beteiligt sein; wichtig ist nur, als Gegensatz zu bisher, dass stets mindestens zwei volle Paare das Gleichgewicht bilden). Gleichgewichtsbedingung ist, wenn kleine Buchstaben die entsprechenden Konzentrationen bezeichnen

$$K = \frac{b_1 \cdot a_2}{a_1 \cdot b_2} \tag{9}$$

Literatur S. 309.

In Lösungen eines reinen Stoffes entsteht der zugehörige Partner in kleiner Menge durch Gleichgewichtseinstellung mit dem Lösungsmittel (Protonenaustausch), das selber das zweite Acidoid/Basoid-Paar liefert (gleich für wässrige oder nicht wässrige Lösungen gültig); die Lösungen reiner Acidoide oder Basoide sind schwach gepuffert und die Mischungen (bei denen die Partner von vornherein in vergleichbaren Konzentrationen gelöst wurden) stark; eine Mittelstellung nehmen die Ampholyte ein.

Der Begriff des Ampholyten erfährt in dieser Darstellung eine ausserordentliche Erweiterung; neben den bisher so benannten Stoffen umfasst er alle mittleren Salze und die Salze aus schwacher Säure mit schwacher Base. (Umkehrung des bisher gebräuchlichen Satzes: Ein Ampholyt ist nichts anderes als das Salz aus schwacher Säure mit schwacher Base, bei dem die beiden entgegengesetzten Funktionen am gleichen Molekül haften.)

Wir wollen nun sehen, welche Stoffe in spezieller Auslegung der allgemeinen Formel (8) als Acidoide, Basoide oder Ampholyte anzusehen sind, wobei die für nicht wässrige Lösungen gültigen Ausdrücke in Klammern gegeben sind.

III. DIE AUSDEUTUNGEN DER ALLGEMEINEN FORMEL

Acidoide sind dem Wasser (Lösungsmittel) gegenüber solche Partikeln, die Protonen an die Wassermoleküle abgeben (an die Protonen-armen Partikeln des Lösungsmittels) und dadurch unmittelbar die Hydroniumkonzentration (die Konzentration der Protonen-reichen Partikeln) über den Wert im reinen Wasser (Lösungsmittel) erhöhen; dabei ist es gleichgültig ob die betrachteten Partikeln Moleküle oder Ionen sind. — Das hervorgehobene Wort „unmittelbar" grenzt die nur als Acidoide wirkenden Partikeln gegen Ampholyte ab, die infolge sekundärer Reaktionen sauer reagieren können.

Anwendung auf Formel (8): A_1 ist das gelöste Acidoid, B_2 Wasser (dessen Konzentration also nicht in Gl. (9) eingehen wird), B_1 der zum gelösten Acidoid gebildete Partner, A_2 ist Hydronium. — Aus Gl. 9 wird

$$K \frac{h \cdot b}{a} = \frac{h^2}{C_a} \qquad (10)$$

wenn C_a die Konzentration des gelösten Acidoids bedeutet und wir die Bedingungen für Zulässigkeit der bekannten Näherungen als gegeben ansehen.

Ist das gelöste Acidoid ein Säuremolekül, so haben wir unverändert in Form und Zahlenwert die bisherige Dissoziationskonstante; und wollen wir, entsprechend der Analogie in Gl. 4, für ein Basenkation als gelöstes Acidoid die gleiche Formel verwenden, dann dürfen wir die Basen nicht mehr durch die fiktive Dissoziationskonstante eines gar nicht existierenden Moleküls kennzeichnen, sondern wir müssen statt dessen die Konstante des tatsächlich herrschende Gleichgewichtes geben, das ist, in der alten Ausdrucksform: die Hydrolysenkonstante des Basenkations.

Literatur S. 309.

Das ist die grundsätzliche Neuerung, die hier vorgeschlagen werden soll. Man verzichte auf die unberechtigte Parallele zwischen der Dissoziation von Säuren und Basen, die zu zwei verschiedenen Klassen von Dissoziationskonstanten führt, und gebe statt dessen einheitlich die Gleichgewichtskonstanten von Acidoid/Basoid-Systemen, wie dies Tabelle I zeigt und wie wir das für Redox-Systeme von jeher gewohnt sind.

TABELLE I

GLEICHGEWICHTSEXPONENTEN VON ACIDOID/BASOID-SYSTEMEN

No.	Acidoid	Basoid	p*K*	vgl. No.
1	Oxalsäure	Oxalat(1)	1.19	10
2	Phosphors.	Phosphat(1)	1.96	19,25
3	Glycinium	Glycocoll	2.35	22
4	Weinsäure	Tartrat(1)	2.96	8
5	Citronens.	Citrat(1)	3.08	12,16
6	Ameisens.	Formiat	3.75	
7	Milchsäure	Lactat	3.86	
8	Tartrat(1)	Tartrat(2)	4.16	4
9	Bernsteins.	Succinat(1)	4.18	17
10	Oxalat(1)	Oxalat(2)	4.22	1
11	Anilinium	Anilin	4.33	
12	Citrat(1)	Citrat(2)	4.75	5,16
13	Essigsäure	Acetat	4.76	
14	Chinolinium	Chinolin	5.00	
15	Pyridinium	Pyridin	5.36	
16	Citrat(2)	Citrat(3)	5.40	5,12
17	Succinat(1)	Succinat(2)	5.55	9
18	Kohlensäure	Carbonat(1)	6.46	23
19	Phosphat(1)	Phosphat(2)	7.12	2,25
20	Borsäure(2)	Borat	9.11	
21	Ammonium	Ammoniak	9.26	
22	Glycocoll	Glycolat	9.78	3
23	Carbonat(1)	Carbonat(2)	10.36	18
24	Äthylammonium	Äthylamin	10.74	
25	Phosphat(2)	Phosphat(3)	12.32	2,19

Die Systeme sind nach abnehmender Acidität geordnet (Zahlenwerte[2]), genau wie Redoxsysteme nach den Potentialen. Man hat also unmittelbar einen Überblick über ihre relative Lage, sieht sofort, welcher Puffer etwa für ein bestimmtes pH geeignet ist, usw. Die letzte Spalte vermittelt den Zusammenhang zwischen anschliessenden Systemen mehrwertiger Paare. — Für grössere Tabellen wird man zur Ergänzung einen alphabetischen Index brauchen, der auf die Nummern verweist, um das Auffinden einer bestimmten Säure oder Base zu erleichtern; diese kleine Erschwerung dürfte den grossen Vorteilen gegenüber kaum ins Gewicht fallen.

Tun wir das, so können wir die pH-Werte in Acidoidlösungen stets nach der Formel finden:

(11) $h = \sqrt{K \cdot C_a}$ $\quad$ pH $= \frac{1}{2}$ (pK — log C_a)

Basoide sind dem Wasser (Lösungsmittel) gegenüber solche Partikeln, die Protonen binden und dadurch die Konzentration an Hydronium (an den Protonenreichen Partikeln des Lösungsmittels) unmittelbar unter den Wert im reinen Wasser (Lösungsmittel) herabsetzen; es ist gleichgültig, ob die Partikeln Moleküle oder Ionen sind.

In Anwendung auf Gl. 8 haben wir: A_1 ist Hydronium, B_2 das gelöste Basoid, A_2 das aus ihm im Gleichgewicht gebildete Acidoid und B_1 Wasser. Es bedarf keines Beweises weiter, dass wir zu der „Hydrolysenkonstante eines Säureanions" kommen, so dass die für diesen Fall abgeleitete Formel nun auch für gelöste Basen-Moleküle gilt.

Ein Ampholyt in der nun verallgemeinerten Bedeutung ist dadurch gekennzeichnet, dass er zunächst ohne Mitwirkung des Lösungsmittels disproportionieren kann, indem eine Partikel ein Proton an eine gleiche abgibt; damit wird die abgebende der ursprünglichen gegenüber zum Basoid und die aufnehmende zum Acidoid. Ob die Partikeln ungeladen (Moleküle oder Zwitterionen) oder geladen sind (Kationen oder Anionen), spielt keine Rolle; ein Ampholyt liegt immer vor, wenn in Gl. 8 Y = XH (also YH = XH_2) und $n = i$ ist, typisch z.B. im Wasser. Und sowohl das in der Disproportionierung des gelösten Ampholyten gebildete Acidoid wie das ebenso entstehende Basoid muss mit den Ampholytpartikeln und Hydronium im Gleichgewicht sein; daher sind pH-Werte in Ampholytlösungen durch zwei Gleichgewichtskonstanten bestimmt.

Ohne weitere Ableitung ist es klar, dass *in allen* Fällen die vier bisher auf „Säuren" und ihre Derivate angewandten Formeln in folgender Form gelten. Der gelöste Stoff ist

(12) ein Acidoid: pH $= \frac{1}{2}$ (pK — log C_a)
(13) ein Basoid: pH $= \frac{1}{2}$ (pW + pK + log C_b)
(14) ein Ampholyt: pH $= \frac{1}{2}$ (pK_1 + pK_2)
(15) eine Puffermischung: pH = pK — log C_a + log C_b

Diese „Näherungsformeln" beruhen bekanntlich auf zwei vereinfachenden Voraussetzungen: Erstens soll, am Beispiel des Acidoids, die im Gleichgewicht gebildete Basoidmenge klein sein neben der Konzentration des gelösten Stoffes, so dass wegen $b \ll Ca$ für $a = C_a - b = C_a$ gesetzt werden kann. Diese Bedingung ist um so schlechter erfüllt je stärker das Acidoid und je grösser seine Verdünnung ist. — Zweitens aber wird vorausgesetzt, dass die zunächst entstehenden Gleichgewichtsprodukte, Basoid und Hydronium, ihre an sich gleichen Konzentrationen nicht durch irgendwelche Folgereaktionen ändern, daher $h = b$; nun muss aber die Erhöhung der Hydroniumkonzentration eine Vereinigung von Hydronium und Oxhydril hervorrufen; damit kann b nicht gleich h bleiben, sondern es muss gleich h vermehrt um den Betrag der verschwundenen OH^--Ionen sein: $b = h + \sqrt{W} - W/h$. $b = h$, unsre Näherung, finden wir also für $h \gg \sqrt{W}$. Nur in verdünnteren Lösungen schwächerer Acidoide wird diese Bedingung nicht erfüllt sein. In fast allen praktisch irgendwie wichtigen Fällen wird daher höchstens eine der beiden Näherungen unzulässig sein; welche, das sieht man sofort aus der jetzt so einfachen Näherungsrechnung, und vielfach hat man dann auf Grund des ersten, angenäherten Ergebnisses eine ganz einfache Möglichkeit, sofort und ohne Anwendung komplizierterer

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Formeln, zum genauen Wert zu kommen. Hat man gefunden, dass $a = C_a - b = C_a - h$ nicht gleich C_a gesetzt werden kann, weil h nicht $\ll C_a$ ist, dann weiss man, dass man h etwas zu hoch gefunden hat; man zieht also von C_a *etwas weniger als das gefundene* h ab und wiederholt mit diesem richtigeren Wert von a die Rechnung. Meist stimmt, bei einiger Übung, dieser zweite errechnete Wert mit der ersten Verkleinerung von h auf einige Hundertstel überein; wenn nicht, sicher die nächste Rechnung. — Auch wenn man von vornherein weiss, dass eine der Näherungen nicht gelten kann, und deshalb nach einer der bekannten genauen Formeln rechnen will, bleibt unser Vorteil erhalten: auch von diesen bleiben nur die ,,Säureformeln'' übrig.

Völlig verschieden in Zielsetzung und Ergebnissen von der vorliegenden Entwicklung ist eine kürzlich erschienene Arbeit von Eeckhout[3]; er verzichtet auf eine klärende Umformung der Bezeichnungen und sagt daher (S. 206, oben): ,,According to Brönsted the cation A^+ reacts as an acid, the anion B^- is a base, but can behave also as an acid.'' Dafür gibt Eeckhout eine ,,general equation'', die für alle Salze A_aB_b gelten soll, auch saure, basische oder gemischte, wie die mittleren Phosphate, Natrium-Ammonium-Carbonat, usw., bei allen Verhältnissen der beteiligten Dissoziations — oder Hydrolysen-Konstanten und in allen Verdünnungen. — Selbstverständlich fallen dann von den zahlreichen Korrektionsgliedern der Einheitsformel je nach Sachlage eins oder mehrere heraus, und so löst auch diese sich wieder in eine Mehrheit auf. Das Verfahren ist also diametral entgegengesetzt dem hier skizzierten: es rechnet erst mit einer komplizierten Formel und stellt dann fest, welche der vereinfachten man statt dessen verwenden kann, während hier die Überschlagsrechnung mit einer sehr einfachen Formel ergibt, welche Korrekturen man etwa für ein genaueres Ergebnis anbringen muss. — Was aber die Genauigkeit der Ergebnisse anbelangt, so muss es bedenklich scheinen, dass Eeckhout für Natriumsulfat, ein nach weit verbreiteter Meinung neutral reagierendes Salz, in 0.1 M Lösung: pH = 7.35 errechnet (S. 210) und für $NaHSO_4$, 0.01 M zunächst pH = 1.85 und dann ,,a more accurate value'': pH = 2.14. Nun zerfällt das Salz, wie auch Eeckhout annimmt, völlig in seine Ionen; es muss daher pH = $-\log h$ = 2.00 sein; ein kleinerer Wert ist völlig undenkbar. Rechnet man aber mit Ionenaktivitäten so erhält man $\mathrm{pH}_a = 2.09$ (nicht 2.14).

Wir bleiben also bei den einfachen Formeln 12, 13 und 14, und definieren in den Ausdrucksformen der klassischen Theorie, als

Acidoide: die Säuren und die gesättigten Salze schwacher Basen;

Basoide: die Basen und die gesättigten Salze schwacher Säuren;

Ampholyte: was bisher genannt wurde und die mittleren Salze mehrwertiger Säuren oder Basen, sowie, für pH-Rechnungen, die Salze aus schwacher Säure mit schwacher Base.

IV. ANALYTISCHE ANWENDUNGEN

Es war üblich zwischen alkalimetrischen und azidimetrischen, zwischen Sättigungs- und Verdrängungstitrationen zu unterscheiden, also vier getrennten Arten. Jetzt bleiben uns zwei Arten: auf Endprodukt, d.h. Acidoid oder Basoid, gleichgültig ob dabei eine Säure oder Base gesättigt oder verdrängt wird, und auf Zwischenprodukt, d.h. Ampholyt, also wiederum eine schätzbare Vereinfachung, die wesentliche Zusammenhänge klarer als bisher hervortreten lässt.

Zunächst ersehen wir aus Gl. 12 und 13, wenn wir mit pH_a das pH eines Acidoids von bestimmter Konzentration und mit pH_b das pH des entsprechenden Basoids in gleicher Konzentration, C bezeichnen:

(16) $$pH_b - pH_a = 7 + \log C$$

Ich glaube nicht, dass dieser Befund irgendwo bisher so klar abgeleitet und ausgesprochen wurde. Normale Lösungen von Essigsäure und Acetat, Borsäure und Metaborat*, Cyanwasserstoff und Cyanid* differieren um 7 in ihren pH-Werten, trotz der Verschiedenheiten in den „Dissoziations"-Konstanten, und ebenso Ammoniak und Ammoniumchlorid, Pyridin und Pyridinium, usw. Zehntelnormale Lösungen differieren um 6, usw.

Mit Tabelle I und den Formeln 15 und 16 lässt sich für jede Titration in einfachster Weise das richtige End-pH finden. Z.B. (A und B in der Tabelle deuten an, ob auf Acidoid oder Basoid titriert wird):

TABELLE II

END-pH VON TITRATIONEN

	Titriert wird:	Gebildet wird:	Titr.-art	End-konz.	End-pH
a)	Essigsäure	Acetat	(B)	*n*/20	7 + 2.38 — 0.65 = 8.73
b)	Ammoniak	Ammoniumsalz	(A)	*n*/100	4.63 + 1 = 5.63
c)	Anilin	Aniliniumsalz	(A)	*n*/20	2.16 + 0.65 = 2.81
d)	invers		(B)	*n*/20	7 + 2.16 — 0.65 = 8.51
e)	Borsäure	Borat	(B)	*n*/10	7 + 4.55 — 0.5 = 11.05
f)	invers		(A)	*n*/10	4.55 + 0.5 = 5.05

Von diesen Titrationen sind einige acidimetrische und andere alkalimetrische; a, b, c und e sind Sättigungs- dagegen d und f Verdrängungstitrationen; das macht nun alles keinen Unterschied mehr; neben der Gleichgewichtskonstante aus Tabelle I ist nur noch zu berücksichtigen, ob das Endprodukt der Titration sauer reagiert oder alkalisch, also der Konzentrationslogarithmus bei der Berechnung des pH-Wertes abzuziehen oder zuzuzählen ist.

V. DIE UMSCHLAGSSCHÄRFE

Ich habe kürzlich dargelegt[6], dass ohne Rücksicht auf die übliche Unterteilung in Fällungs-, Redox-, Komplexbildungs- oder acidimetrische Titrationen die Pufferung am Endpunkt einer Titration einer bestimmten Konzentration proportional ist, die wir deshalb die Kennkonzentration nennen können. Diese Konzentration ist bestimmt durch den Anteil an den Reaktionspartnern (Stoff und

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* Nur in ziemlich konzentrierten Lösungen; in verdünnten gelten die Näherungen nicht mehr.

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Reagens), die am Endpunkt, infolge der Unvollständigkeit der Titrierreaktion, noch frei vorhanden sind, oder, vom Punkte der Reaktionsprodukte aus gesehen, gleich der Konzentration des „umgesetzten Teils" dieser Produkte in der Endlösung. Die Umschlagsschärfe ist der Pufferung und somit der Kennkonzentration umgekehrt proportional.

Bei Titrationen auf Acidoid ist die Kennkonzentration gleich h_0, und auf Basoid gleich oh_0 (Index null, weil kein Überschuss an Stoff oder Reagens vorhanden ist).

Bei einer Titration von starker Lauge gegen starke Säure ist die Kennkonzentration $h_0 = oh_0 = 10^{-7}$; die Umschlagsschärfe ist also bei den oben angeführten Titrationen in folgendem Mass geringer:

a) 54 b) 23 c) 15000 d) 32 e) 11000 f) 89

Was besonders bemerkenswert erscheint, ist das Verhältnis der Umschlagsschärfen, also der erreichbaren Genauigkeiten, bei den inversen Paaren c und d, e und f; in beiden Fällen ist, in der klassischen Ausdrucksform, die Verdrängungstitration ausserordentlich viel genauer als die Sättigungstitration. In unsrer Verallgemeinerung müssen wir fragen: Wann ist bei einem bestimmten Acidoid/Basoid-Paar die eine oder die andere Komponente genauer als die andere zu titrieren?

Die Antwort ist in der neuen Darstellung so selbstverständlich, dass sie nicht einmal einer Ableitung bedarf: Für pK < 7 ist das Acidoid genauer zu titrieren und für pK > 7 das Basoid; je weiter die Werte von 7 entfernt liegen, desto grösser wird der Unterschied. Natürlich sind die Fälle nicht häufig, in denen wir zwischen den beiden Möglichkeiten wählen können; immerhin gibt es selbst bei den einwertigen Säuren und Basen einzelne (siehe die eben erwähnte Arbeit). Besonders wichtig aber wird das Problem, sobald Ampholyte in Frage kommen.

Die Umschlagsschärfe in Ampholytlösungen. Es ist einleuchtend, dass für Ampholytlösungen die eben gegebene Regel keine Geltung haben kann: pH $= 7$ haben wir im reinen Wasser und genau so in einer Ammonacetatlösung, die ihr pH nur schwierig ändert. pH ~ 4.9 haben wir in einer etwa $n/30$ Lösung von Ammonchlorid mit ausgezeichnetem Umschlag und im primären Succinat, dessen Bildung titrimetrisch nicht zu erfassen ist. Grund hierfür: in der Ampholytlösung ist $h_0 = \sqrt{K_1 \cdot K_2}$, die Pufferung aber proportional der Konzentration der Disproportionierungsprodukte, $a_0 = b_0 = C\sqrt{K_2/K_1}$ (Ableitung genau wie in der früheren Arbeit; der genaue Wert ist $a_0(1+\alpha)$ wobei α der grössere der beiden Werte, h_0 oder oh_0 ist; es ist immer $\alpha \ll a_0$).

So kommt es, dass unabhängig von den pH-Werten auf manche mittleren Salze mehrbasischer Säuren recht gut und auf andere überhaupt nicht titriert werden kann; vgl. Tabelle III.

P_t ist der pH-Wert in der Lösung der reinem Stoffe, die nach steigendem Abstand dieses Wertes vom Neutralpunkt geordnet sind. In Lösungen von Acidoiden oder Basoiden würde der Fehler bei gleichem Irrtum im pH proportional

TABELLE III

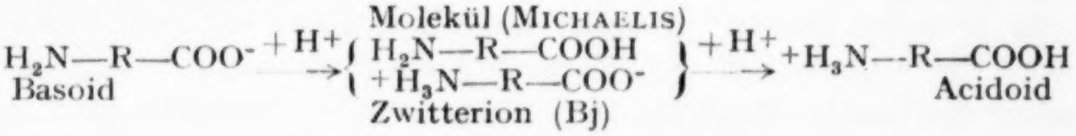
PH-WERTE UND PUFFERUNG MITTLERER SALZE MEHRBASISCHER SÄUREN

Salz:	p_t	$\|7-p_t\|$	% Fehler bei $\|pH-p_t = 0.1\|$
Bicarbonat	8.41	1.41	0.7
Succinat, prim.	4.86	2.14	1
Phosphat, prim.	4.54	2.46	0.1
Phosphat, sec.	9.76	2.76	0.12
Tartrat, prim.	3.56	3.44	6.3
Oxalat, prim.	2.70	4.30	15

zu diesem Abstand zunehmen; hier ist dies durchaus nicht der Fall, wie die letzte Spalte zeigt.

VI. ÜBER AMINOSÄUREN UND INDIKATOREN

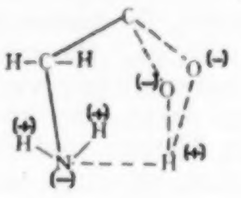
Hinsichtlich der Konstitution der Acidoid- und Basoidform von Aminosäuren ist keine Kontroverse möglich, dagegen hat eine solche hinsichtlich der Ampholytform stattgefunden; es herrscht wohl Einigkeit darüber, dass sie zu gunsten von BJERRUM[7] und gegen MICHAELIS[5] entschieden ist. — Das folgende Schema zeigt die beiden Auffassungen:

(28) 

$$\underset{\text{Basoid}}{H_2N{-}R{-}COO^-} \xrightarrow{+H^+} \underset{\text{Zwitterion (Bj)}}{\overset{\text{Molekül (Michaelis)}}{\left\{\begin{matrix} H_2N{-}R{-}COOH \\ {}^+H_3N{-}R{-}COO^- \end{matrix}\right\}}} \xrightarrow{+H^+} \underset{\text{Acidoid}}{{}^+H_3N{-}R{-}COOH}$$

Nach BRÖNSTED ist nun die Acidoidform der Aminosäure einfach wie eine zweibasische Säure zu behandeln, von der nach einander zwei Protonen abgegeben werden; diese Auffassung hat so grosse Vorzüge, dass sogar Handbücher bei den Aminosäuren die „Säurekonstanten nach BRÖNSTED" anführen[2]; natürlich müssen sie ausserdem, oder in erster Linie, die „Molekülkonstanten nach MICHAELIS" bringen (die sicher sinnwidrig aber älteren Organikern wohl die einzig geläufigen sind) und die „Zwitterionskonstanten nach BJERRUM", zahlenmässig richtig, wenn man die Lehre von der Dissoziation von Säuren und Basen in der klassischen Form beibehält.

Mit der Annahme der BRÖNSTEDschen Formulierungen verliert die alte Kontroverse überhaupt ihre Grundlage, denn nun kommt sie einem Streit darüber gleich, welches der beiden Protonen aus der Äpfelsäure zuerst abdissoziert; auch in dieser sind ja die beiden Protonen an verschiedene Gruppen gebunden da ihre Formel unsymmetrisch ist: $HOOC{-}CH_2{-}CH{\cdot}OH{-}COOH$. Wenn aber jemand, der von der Wesensverschiedenheit eines Säure-Protons und eines Ammonium-Protons durchaus nicht loskommen kann, anführen sollte, dass diese Frage beim primären Malat gleichgültig beim Glycocoll aber von hohem Interesse sei, so ist ihm entgegenzuhalten, dass nach den jetzigen, gut gegründeten Anschauungen weder die Formel nach MICHAELIS noch die nach BJERRUM den Sachverhalt völlig deckt: Das noch abdissoziierbare Proton im Glycocoll ist sicher nicht mit einem der negativen Pole fest verbunden, sondern es nimmt eine Gleichgewichtsstellung zwischen beiden ein, etwa der Formel entsprechend:



Ein Grund mehr, die Gleichgewichtskonstanten von Ampholyten (im klassischen Sinne, also besonders Aminosäuren) in der BRÖNSTEDschen Form zu geben und somit auch die Gleichgewichtskonstanten von Ammoniumionen/Aminen.

Indikatoren. Auch hier bringt die empfohlene Darstellungsform so viel grössere Folgerichtigkeit und Klarheit, dass es genügt einige wenige Beispiele anzuführen, um dies hervortreten zu lassen.

Methylrot geht zwischen den pH-Werten 4.4 und 6.2 aus der Basoid- in die Ampholyt-Form über (gelb-rot); pI = 4.88 (Zahlenwerte: 8), (halb Basoid, halb Ampholyt); eine zweite Umwandlung, Ampholyt/Acidoid, mit Umschlag zu einem etwas verschiedenen Rot, erfolgt bei etwas stärker saurer Reaktion, was bei Titrationen weder stört noch überhaupt bemerkt wird, aber die genaue Bestimmung des pI erschwert hat [9].

Methylorange. Basoid und Ampholyt gelb, Acidoid rotorange, Umschlag zwischen 3.1 und 4.4; pI = 3.39.

Thymolblau. Acidoid/Ampholyt — rot/gelb zwischen 1.2 und 2.8; pI = 1.52; Ampholyt/Basoid — gelb/blau zwischen 8.0 und 9.6; pI = 8.89.

Phenolphthalein. Je nachdem man die in starker Lauge erfolgende Umwandlung in ein farbloses, dreiwertiges Anion als praktisch unwesentlich weglassen oder als theoretisch interessant berücksichtigen will hat man zu sagen: Acidoid und (erster) Ampholyt farblos, Übergang zum roten Basoid (bzw. zweiten Ampholyten) zwischen 8.2, bei hoher und 10.0 bei geringer Indikatorkonzentration; pI = 9.50. (Bei Berücksichtigung der letzten Umwandlung: Basoid farblos; Übergang erfolgt nur in starker Lauge.)

Mir scheint, dass mit dieser funktionellen Beschreibung der Veränderungen im Ladungszustand der Indikatoren eine wertvollere Klärung der Begriffe erreicht wird, als mit der mechnischen Einteilung nach ,,Indikatorsäuren" (Nitrophenole, Phthaleine, Oxyazofarbstoffe) und ,,Indikatorbasen" (Aminoazofarbstoffe, Dimethylaminophenazinchlorid, etc.). Ob im Umschlag eine Säure in ihr Anion oder ein Kation in die Base übergeht, ist für die Lage des Umschlags, die strukturellen Umwandlungen, die die Farbänderung erzeugen, und die zweckmässige Beschreibung des Vorgangs ohne Belang.

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ZUSAMMENFASSUNG

Nach der klassischen Theorie ,,dissoziieren" schwache Säuren und Basen *im* Wasser, während ihre Salze *durch* das Wasser ,,hydrolysiert" werden; im ersten Prozess soll das Wasser nur physikalisch mitwirken: seine hohe Dielektrizitätskonstante vermindere die elektrostatische Anziehung der Ionen; am zweiten Vorgang dagegen nehme das Wasser auch chemisch Teil.

Wir wissen heute, dass diese Vorstellungen unhaltbar sind und dass stets eine Reaktion mit dem Wasser stattfindet. In dieser hydrolysieren Säurenmoleküle und Basenkationen in gleicher Weise, während Basenmoleküle und Säureanionen wieder analog zu einander, aber völlig verschieden von dem ersten Vorgang mit dem Wasser reagieren. Die klassischen Analogien sind also unberechtigt und müssen durch andere ersetzt werden. Die Säuren und Basen dürfen nicht durch ,,Dissoziations"-Konstanten besonderer Art, sondern beide müssen durch eine einzige Art von Gleichgewichtskonstanten gekennzeichnet werden.

Berücksichtigt man dies, so werden Ableitungen von pH-Werten wesentlich vereinfacht: es verschwindet über die Hälfte der bisher nötigen Formeln und der Inhalt der verbleibenden tritt klarer hervor. Der Übergang von der Betrachtung wässriger Lösungen zu nicht-wässrigen wird vereinfacht. Es erscheinen wertvolle Analogien zu den Redox-Systemen.

SUMMARY

According to the classic theory weak acids and bases dissociate *in* water whilst their salts are hydrolysed *by* water; in the first process the water is supposed to perform a merely physical action as its high dielectrical constant diminishes the electrostatic attraction between the ions; in the second process the water is said to participate chemically.

We know nowadays these conceptions to be obsolete: there is always a reaction with the water. In these reactions the molecules of acids and the cations of bases are hydrolysed in the same manner, whilst the molecules of bases and the anions of acids react analogously to each other but differently from the first process. The analogies as formulated up to now are incorrect and different ones have to supersede them. We shall not establish dissociation constants of a different kind for acids and bases, but identical equilibrium constants for both of them.

By this development the calculation of pH-values is greatly simplified, as more than half of the actual formulae disappear and the meaning and interpretation of the remaining formulae are self-explanatory. The transition from aqueous to non-aqueous solutions is easy. Important analogies to the redox systems are established.

RÉSUMÉ

Suivant la théorie classique, les acides et les bases faibles sont dissociés *dans* l'eau, tandis que ses sels sont hydrolysés *par* l'eau; dans le premier cas on attribue à l'eau un rôle purement physique: par sa constante diélectrique élevée elle fait diminuer l'attraction électrostatique des ions, tandis que dans le second on suppose une participation chimique des molécules d'eau.

Nous savons aujourd'hui que ces idées sont incorrectes et que des réactions chimiques du composé dissous ont lieu avec l'eau. Dans ces réactions, les molécules des acides et les cations des bases sont hydrolysés de la même manière, tandis que les molécules des bases et les anions des acides présentent une réaction inverse de la première, mais équivalente. Au lieu d'attribuer aux acides et aux bases deux classes différentes de ,,constantes de dissociation", il faut les caractériser par des ,,constantes d'équilibre" de forme identique pour tous les deux.

Ayant égard à ces notions, on simplifie énormément le calcul des valeurs du pH; de neuf formules antérieures il ne restent que quatre dont l'interprétation est extrêmement simple. Il est facile de passer de l'étude des solutions aqueuses à celle des non-aqueuses. Des analogies importantes avec les systèmes rédox sont établies.

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RESUMEN

Según los conceptos de la teoría clásica los ácidos y las bases débiles ,,disocian" *en* el agua, en tanto que sus sales son hidrolizadas *por* el agua, suponiéndose que en el primero de los procesos mencionados, el agua tenga exclusivamente une acción física: su elevada constante dieléctrica haga disminuir la atracción electrostática de los iones; en el segundo proceso se supone además una participación química del agua.

Sabemos hoy en día que estos conceptos no pueden mantenerse, ya que siempre ocurre una reacción química con el agua. En ésta, las moléculas de los ácidos y los cationes de las bases se hidrolizan idénticamente, en tanto las moléculas de las bases y los aniones de los ácidos reaccionan nuevamente en forma similar pero que mucho dista de las reacciones anteriores. Las analogías clásicas son incorrectas, por consiguiente, y deben sustituirse por otras. No es correcto caracterizar los ácidos y las bases por constantes de ,,disociación" de diferentes clases, sino que para ambos existe una sola clase de constantes de ,,equilibrio".

Con esto, el cálculo de valores del pH se simplifica enormemente, ya que más que la mitad de las fórmulas actuales desaparece y las restantes se interpretan con mayor facilidad. Además se simplifica el estudio de las soluciones no acuosas y se establecen analogías valiosas con los sistemas redox.

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„RAPIDANALYSE" TROCKENREAGENZIEN FÜR ANALYTISCHE ZWECKE

von

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Während geringste Mengen, selbst Bruchteile eines Gamma, verschiedenster Substanzen sich leicht nachweisen lassen ist dabei der Verbrauch an oft teuren Reagenzien meist zehn bis hundertmal grösser als nötig. Das liegt daran, dass die wenigen Tropfen oder Kubikzentimeter an Reagens aus grossen Vorratsflaschen entnommen werden, wobei der grösste Teil dieser Lösungen unverbraucht verdirbt. Nach dem Prinzip unserer „Rapidanalyse" stellt man Lösungen in der gerade benötigten Menge im Augenblick der Benützung her und zwar aus Material das unbegrenzt lange aufbewahrt werden kann. Wir beschränken uns heute darauf die Benutzung von Imprägnationen löslicher und unlöslicher Träger zu betrachten und diejenige reiner gepulverter Substanzen nebenbei zu erwähnen. Als Grundlage für die praktischen Beispiele hat uns in der Hauptsache das Werk: „*Reagents for Qualitative Inorganic Analysis*" von P. E. WENGER und R. DUCKERT, C. J. VAN NIEUWENBURG UND J. GILLIS gedient, aber auch andere Imprägnationen können angeführt werden.

Was sind Imprägnationen?

Darunter verstehen wir Lösungen oder Aufschwemmungen fester Substanzen die auf einem geeigneten löslichen oder unlöslichen Träger aufgetrocknet wurden. Reagenspapiere sind ein Beispiel dafür, weniger bekannt sind die schwammartigen Glassteinchen (sintered glass granules) die in U.S.A. in weitem Umfange für den Nachweis von Eiweiss im Harn oder auch als Siedesteinchen (boiling stones) gebraucht werden. Sie könnten aber für die verschiensten Nachweise benutzt werden. Ausser diesen kann man Sand, Salze oder Zucker etc. verwenden. Nachstehend geben wir die hervorstechendsten Eigenschaften der verschiedenen Träger an.

1. *Papier*

Dieses kann nur geringe Mengen an aktivem Material enthalten und daher kann man Lösungen durch Einwerfen imprägnierten Papieres nur in beschränk-

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tem Masse herstellen. Es dient daher meist nur als Unterlage für Spottest's. Ein grosser Nachteil ist die oft nur beschränkte Haltbarkeit imprägnierter Papiere.

2. *Granules*

Da uns eine deutsche Bezeichnung für dieses interessante Material nicht bekannt ist, behalten wir die englische Bezeichnung bei. Granules sind schwammartig und bestehen aus reinem SiO_2 falls sie nicht durch Staub verunreinigt sind. Sie sind leicht alkalisch, wie man bei der Imprägnation mit Indikatoren sieht, im übrigen aber ein idealer Träger für fast alle organischen und anorganischen Reagenzien. Sie können ausserdem mit Farbstoffen, Oxydations- oder Reduktionsmitteln oder pH Mischungen imprägniert werden, wobei selbst sehr hygroskopische Substanzen verwandt werden können. Der inerte Träger beeinflusst praktisch keine Reaktion und die einzelnen Körnchen lassen sich stets leicht abtrennen und für Einzelreaktionen verwenden.

3. *Sand*

Dieser muss natürlich erst mit Säuren ausgekocht und gewaschen werden um Kalksalze und andere Verunreinigungen zu entfernen. Er ist dann ganz frei von Alkali, aber enthält oft noch Spuren von Metallsalzen, besonders Eisen. Als Träger für Indikatoren eignet er sich ausgezeichnet, kann aber auch überall dort gebraucht werden, wo die kleinen Verunreinigungen nicht stören.

4. *Salze*

Natriumchlorid, Kaliumsulfat und in besonderen Fällen einige andere Träger, wie Sulfanilsäure oder Natriumsulfanilat, etc. lassen sich gut verwenden. Ihr grosser Vorzug ist, dass sie ohne weiteres und für geringen Preis in grosser Reinheit überall erhältlich sind. Ihr Nachteil, dass das Salz im Laufe der Zeit etwas zusammenbackt und einzelne Körnchen sich nur dann abtrennen lassen, wenn man einen Spatel in dem Vorratsgefäss belässt. Eine Feder aus nichtrostendem Stahl oder etwas Ähnliches aus plastischem Material eignet sich gut dafür. Sie kann im Korken stecken. Salze sind *unlösliche Träger*, was man auf den ersten Blick meist nicht gewahr wird, wenn man Alkohol oder andere Lösungmittel gebraucht die nur die imprägnierende Substanz auflösen. Sie eignen sich daher vorzüglich zur Imprägnation mit den Reagenzien, wie Dithizon, Gallocyanin, Quinalizarin etc. wobei Alhohol zur Lösung gebraucht wird und das Salz als Träger zurückbleibt, ohne an der Reaktion teil zu nehmen.

5. *Organische Substanzen*

Glukose, Saccharose etc. lassen sich in beschränktem Masse an Stelle der Salze benutzen, z.B. für Hämoglobin, wo alle Ionen störend wirken, wenn man den Blutnachweis ausführen will.

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Imprägnierte Träger kann man auch noch in Verbindung mit Mischungen benutzen, oder auch Mischungen allein. In dieser Aufstellung scheint uns dann alles enthalten zu sein, was an Trockenreagenzien hergestellt werden könnte und darin inbegriffen wären sogar noch Farbstofftabletten, Trockensera etc.

Herstellung der Imprägnation

Man stelle eine Lösung oder Aufschwemmung des aktiven Materials her und übergiesse damit die gewünschte Menge des geeigneten Trägers und trockne dann entweder bei Zimmertemperatur oder im Trockenschrank. Sehr homogen werden die Imprägnationen, wenn die Lösung gerade vom Träger aufgesaugt wird und keine Flüssigkeit übrig bleibt. Man kann auch erst den ersten Teil der Flüssigkeit verwenden und wenn alles trocken ist, einen weiteren Teil darüber giessen. Kommt es auf gleichmassige Zusammensetzung nicht sehr an, so verwendet man die gesammte Flüssigkeit, wobei ein Teil der aktiven Substanz ungelöst bleiben kann. Nach dem Trocknen kleben die einzelnen Teilchen doch so fest am Träger, dass die Imprägnation eine fast homogene Mischung bildet, die sich von einfachen Mischungen durch ihre Beständigkeit und meist auch durch die Farbe unterscheiden lässt. Auch durch langes Schütteln trennt sich eine Imprägnation nicht leicht in ihre Bestandteile.

Benutzung der Imprägnation

Man werfe einfach ein oder mehrere Körnchen der imprägnierten Substanz in das geeignete Lösungsmittel und schon ist das Reagens fertig. Es ist stets frisch und kann in beliebiger Menge in Sekunden hergestellt werden. Indikatoren, die nicht haltbar sind, wirft man einfach als Sandimprägnation in den Kolben wo die Titration ausgeführt wird, z.B. Murexid bei Komplexontitration, etc.

Die so sehr verdünnten 0.01%igen Lösungen von Dithizon, von Kupfersulfat, von Diphenylamin, etc. bereitet man in gleicher Weise und benutzt sie genau so, wie man die aus der Vorratsflasche entnommenen gebraucht hat.

Die von FEIGL zum Vergleich empfohlenen Lösungen, die ein Gramm pro Liter enthalten, lassen sich vermutlich mit genügender Genauigkeit durch Abtrennen oder Abwiegen von einem halben Gramm Trockenreagens und übergiessen mit der entsprechenden Menge an Lösungsmittel herstellen. Der Inhalt des Schraubverschlusses kann als Mass dienen, wenn man das erste Mal diesen Inhalt gewogen hat.

Die Haltbarkeit der Imprägnationen ist meist so gut wie die der reinen feinst gepulverten Substanzen, wenn man nicht weniger als ein Prozent an aktivem Material im Reagens belässt. Sind konzentriertere Lösungen, z.B. von fünf bis zehn Prozent herzustellen, so verwendet man am besten die reinen Substanzen

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feinst gepulvert, die meist auch in Sekunden in Lösung gehen. Mit Ausnahme der Säuren und der Alkalien, die normalerweise flüssig sind, kann man den grössten Teil unserer empirischen Lösungen mit vorzüglichem Erfolg durch trockene Substanzen ersetzen, die erst im Moment des Gebrauches in Lösung gebracht werden. Im allgemeinen wird man fünfzig und selbst hundertmal mehr Reaktionen mit demselben Material ausführen können als früher, selten etwas zum Waschen haben und auch teure Reagenzien für billigsten Preis zur Verfügung haben.

Ein besonderer Vorzug ist, dass das geringe Volumen der trockenen Reagenzien es gestattet, sogenannte „Mikrolaboratorien" herzustellen, d.h. alles für die Analysen notwendige Material inklusive die Filter, Trichter, etc. in einer kleinen Schachtel unterzubringen, die leicht transportabel ist und praktisch doch dasselbe bieten kann, wie ein umfangreiches, recht gut eingerichtetes Labor für dieselben Untersuchungen. Wir haben bisher hauptsächlich auf klinischem Gebiet gearbeitet, wo die Verwendung von Trockenreagenzien in Zusammenhang mit einer geeigneten Arbeitstechnik, die wir als „Rapidanalyse" weitgehend veröffentlicht haben, die Herstellung von „Mikrolaboratorien" gestattet. Wichtig ist, dass jeder sich diese Mikrolaboratorien selbst herstellen kann, da die Reagenzien und die Technik nur Abarten des alt Bekannten sind. Sie sind an vielen Orten mit grossem Erfolg seit längerer Zeit im Gebrauch. Hier wenden wir nun dieselben Prinzipien auf das technisch-analytische Feld an und überlassen es jedem, einen Versuch anzustellen, besonders da wir nicht alle hier zum Versuch empfohlenen Produkte aus Mangel an Chemikalien haben herstellen können. Wir wollen erwähnen, dass „Mikrolaboratorien" sich durch Hinzufügen einiger Instrumente, wie Zentrifuge, Photometer, Mikroskop, etc. sich in gewöhnliche Laboratorien umwandeln lassen, aber stets ausserordentlich viel billiger und kleiner, als die klassichen Laboratorien ausfallen werden.

Da es am Schwierigsten ist, sich darüber klar zu werden, welche Produkte erfolgreich gebraucht werden können, geben wir nachstehend eine Aufstellung derjenigen, die es lohnt zu probieren. Die meisten beziehen sich auf das oben genannte Werk von Wenger und die Seitenzahl bezieht sich auf die englische Ausgabe. Es gibt aber noch zahlreiche andere Produkte ähnlicher Art, die um so vorteilhafter in ihrer neuen Anwendungsweise sind, je seltener sie gebraucht werden, oder je teurer und je weniger haltbar sie sind. Von Puffermischungen zur sofortigen Herstellung von Standards, etc. allein kann man wenigstens ein halbes hundert anführen.

Die Herstellung und Aufbewahrung erfolgt am besten indem man ein Gramm der Substanz als Imprägnation für den Inhalt eines Penizillinfläschchens (25 ml) an Träger verwendet und die fertige Imprägnation wieder darin aufbewahrt.

Reagenzien die sich zur Imprägnation auf Granules, auf reinem Sand oder auf Salz eignen.

Ein Gramm an Substanz auf zwanzig Gramm Träger ist ein meist günstiges Verhältnis.

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Seite	Substanz	Träger Granules	Salz
8	*p*-Dimethylaminobenzylidenrhodanin	+	+
9-263-277	Diphenylcarbazid	+	+
17-50-66	Rubeansäure	+	+
25	Bleiacetat	+	+
27	Cinchonin	+	
31	Cadion	+	+
31	Kaliumhydroxyd	+	
33	sym-Diphenylcarbazid	+	+
39	Rhodamin B auf Kaliumchlorid 0.5 auf 150		
41	Gallocyanin	+	
44-116	Dimethylglyoxim	+	+
45	Cacothelin	+	
67	Diphenylhydrazin	+	
71-172	Kupfersulfat	+	
74-250	Benzidin	+	
75	Phenolphtalein	+	
75	Natriumhydrat	+	
76-158	Chinalizarin	+	
82-113	Dipyrridyl	+	
87-128	8-Hydroxichinolin	+	
89-91	Ferrichlorid	+	
10	Alizarinsulfonat	+	
11	Natriumpurpurin-3-sulfonat	+	
12	Morin	+	+
15	*o*-Phenantrolin	+	
20-173	Kobaltchlorid	+	
124	Guyacharz	+	
125	Strychnin	+	
130	Querzetin	+	+
138	Jod (Jodid-Jodat)	+	
149	*p*-Dimethylamino-4-azophenylarsonsäure	+	
155	Alizarin	+	+
157-175	*p*-Nitrobenzol-azo-orcinol	+	
161	Wismuthnitrat	+	
164	Cochenilletinktur	+	
176	*p*-Phenetidinhydrochlorid	+	
178	Silbernitrat	+	
189	Zinksulfat	+	
192	Nitrosonaphtol	+	+
194	2-Nitroso-4-sulfo-1-naphtol	+	
197	Cyclohexandion-dioxim	+	
214	Kupfernitrat	+	
218	Magneson	+	+
220	Titangelb	+	+
247	Nesslerreagens (Kalium-Quecksilberjodid)	+	
274	Fluorescein	+	
274	Kaliumpermanganat	+	
274	Bleisuperoxyd	+	

Ausser den hier genannten Imprägnationen, die sich auf das Buch von WENGER beziehen, gibt es noch zahlreiche andere von denen wir einige anführen, die alle am besten auf Granules gemacht werden.

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Oxydationsgranules mit einem geeigneten Peroxyd Reduktionsgranules.

Vanillin	Günsburgsreagens
Phlorogluzin	Reaktion nach Kreis für Fette
Kuprooxyd	erlaubt Folin-Wu Reaktion auszuführen und daher Photometer nach einem geeichten Apparat zu standardisieren ohne die Analyse zu machen.
Naphtylamin	auf Sulfanilsäure 0.1:0.5 vorzüglich zum Nitritnachweis.

Dazu kommt eine lange Serie von sogenannten „Pantestprodukten". Das sind Imprägnationen, die es gestatten, sofort eine positive Reaktion zum Vorgleich oder zur Demonstration auszuführen. Sie ersetzen die Beschreibung durch die Analyse und erlauben es auch, die Haltbarkeit der Trockenreagenzien jederzeit zu kontrollieren und ausserdem auch den negativen Blankoversuch zu machen und alles das in etwa ein bis zwei Minuten. Beispiele:

Als „Pantest" für Uranreaktionen kann ein beliebiges Uransalz, das auf Granules imprägniert ist, dienen. Das Anion dient gleichzeitig als „Pantest" für die entsprechende Säure. Prinzipiell kann man jedes Uransalz verwenden, aber in der Praxis bevorzugt man die leicht löslichen Salze. In entsprechender Weise dienen Vanadin-, Eisen-, Blei-, etc. Salze als „Pantest" für das darin enthaltene Metall.

Als „Pantest" für Hämoglobinreagenzien benutzt man Hämoglobin auf Zucker, da Salze falsche positive Reaktionen herbeiführen.

Einige Imprägnationen können gleichzeitig für verschiedene Reaktionen gebraucht werden, z.B. Nitroprussiat auf Natriumchlorid 1:10 ist vorzüglich zum Azetonnachweis, aber eben so gut zum Nachweis des Schwefelwasserstoffes.

Andere Verwendungen sind Imprägnationen von Arabinose oder anderen Zuckern zur Ausführung der Pentosereaktion etc.

Man kann auch fast alle Puffermischungen als Imprägnation benutzen und so den Ablauf zon Reaktionen beeinflussen oder mikroskopische Färbungen beim günstigsten pH ausführen oder kolorimetrische Standards im Moment herstellen.

Eine Abart davon sind Farbstoffe als Imprägnation z.B. Methylenblau oder Malachitgrün zum Nachweis von Ameisensäure resp. von Sulfiten. Dieselben Farbstoffe können aber auch für mikroskopische Färbungen dienen und so ist es möglich, die Ziehlsche Fuchsinlösung durch eine Imprägnation auf Sand mit oder ohne Zusatz von Phenol zu ersetzen. Diese ist leicht transportabel und verschmutzt nichts beim Zerbrechen.

Zum Schluss wollen wir nochmals hervorheben, dass bei der Wahl des Trägers vor allem zu berücksichtigen ist, dass er keine interferierenden Bestandteile enthält, dass also weder der Sand, noch die Granules etwa Spuren von Aluminium

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oder Kalzium enthalten, wenn man auf diese Elemente untersuchen will. Die Granules enthalten meist nur Spuren von Eisen und durch Auskochen mit Säure lassen sie sich wohl auch von diesem und ev. enthaltenem Kalzium befreien. Ein qualitativer Versuch ist unter allen Umständen auszuführen, kostet aber meist wenig Zeit.

Der Chemische Fabrik vorm. Siegfried in Zofingen sprechen wir unseren besonderen Dank aus für die freundliche Übersendung eines beträchtlichen Teiles der in Argentinien nicht erhältlichen Chemikalien und ebenso der Firma R. P. Cargille, 117 Liberty Street, New York 6, die uns alle Granules und einen weiteren Teil der Chemikalien zur Verfügung stellte.

ZUSAMMENFASSUNG

Die Benutzung von Imprägnationen auf einem geeigneten Träger gestattet es, den grössten Teil der heute für qualitative Analysen gebrauchten empirischen Lösungen durch trockene Reagenzien zu ersetzen. Diese sind von unbegrenzter Haltbarkeit, geringstem Volumen und sehr ökonomisch.

SUMMARY

The use of solid reagents for qualitative analyses is proposed, by means of impregnating appropriate carriers. This technique has many advantages and is very economic, it can be used on very small volumes.

RÉSUMÉ

L'auteur propose pour les analyses qualitatives, l'utilisation de réactifs solides imprégnés dans des supports appropriés. Cette technique est très avantageuse et très économique, elle permet de travailler sur de très faibles volumes.

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NEW REACTIONS OF NICKEL AND COBALT WITH IRON-CYANOGEN COMPOUNDS AND A NEW METHOD OF DETERMINATION OF FERRICYAN

by

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It has been known for many years that the white ferrous ferrocyanide is oxidised by the oxygen of the air to Prussian blue and the white cuprous ferrocyanide to the brown cupric ferrocyanide. In the first case the bivalent extra-radical iron changes into the trivalent iron, in the second case the monovalent extra-radical copper changes into the bivalent copper in this oxidation. In what follows two reactions are reported in which the ferrocyan radical is oxidised to ferricyan by the oxygen of the air. It was observed that the light green nickel ferrocyanide is slowly oxidised to the brown nickel ferricyanide in the presence of acids. Experiments on the oxidation of nickel ferrocyanide by the oxygen of the air were carried out in the presence of hydrochloric acid and acetic acid. In all these cases the quantities of ferricyanide formed could be determined. These determinations use the fact that nickel ferricyanide is transformed quantitatively into nickel ferrocyanide and potassium ferricyanide by the addition of potassium ferrocyanide.

$$2\,Ni_3[Fe(CN)_6]_2 + 3\,K_4\,[Fe(CN)_6] = 4\,K_3\,[Fe(CN)_6] + 3\,Ni_2\,[Fe(CN)_6]$$

If the mixture is filtered, the filtrate contains the potassium ferricyanide, which can be titrated with sodium thiosulphate according to MÜLLER AND DIEFENTHAELER[1].

While the white ferrocyanide, as was found earlier[2], is oxidised completely by neutral diluted hydrogen peroxide to the basic Prussian blue $[(HO)_2Fe_2Fe(CN)_6]$, nickel ferrocyanide is not attacked under the same conditions. However, hydrogen peroxide in the presence of acids, oxidises to nickel ferricyanide. Nitrous acid, as well as bromine water, also easily oxidises the ferrocyanide to nickel ferricyanide.

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LUCKOW[3] found that cobalt ferrocyanide precipitated from acid solutions is a green substance, which becomes gradually grayish. This statement is erroneous, because in acid solutions the originally green precipitation changes its colour into a ultramarine blue with a slightly grayish tinge. This substance, which is formed by the oxidation of cobalt ferrocyanide by the oxygen of the air, is very similar to Prussian blue and to Turnbull's blue and could be called cobalt Prussian blue. It gives with alkali a dark, $Co(OH)_3$ containing precipitate, while the filtrate contains potassium ferrocyanide. The blue colour is striking. It is not the mixed colour that could be expected by the addition of the blood-red or purple-red cobalt ferricyanide to the green cobalt ferrocyanide. The blue substance on being treated with $K_4[Fe(CN)_6]$ produces indeed $K_3[Fe(CN)_6]$. But this reaction is not complete because the filtered product is still blue. In the complete reaction the pure cobalt ferricyanide reacts with $K_4[Fe(CN)_6]$ forming green cobalt ferrocyanide and potassium ferricyanide.

$$2\,Co_3[Fe(CN)_6]_2 + 3\,K_4[Fe(CN)_6] = 3\,Co_2[Fe(CN)_6] + 4\,K_3[Fe(CN)_6]$$

This fact can also be proved by iodometric determination of the $K_3[Fe(CN)_6]$ contained in the filtrate.

$Co_2[Fe(CN)_6]$ maintains its green colour if, in the precipitation, such a quantity of sodium chloride is added that part of the sodium chloride remains undissolved. If potassium chloride is used instead of NaCl, the precipitation of $Co_2[Fe(CN)_6]$ maintains a reddish-gray colour.

The blue substance is also formed if mixtures of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ are precipitated with an excess of a cobalt salt, kept at room temperature for some days and shaken sometimes. The originally violet colour changes into a slightly grayish ultramarine blue. This change can also be proved analytically. The mixture of $Co_2[Fe(CN)_6]$, $Co_3[Fe(CN)_6]_2$ and a cobalt salt, if immediately after the precipitation an excess of $K_4[Fe(CN)_6]$ is added, is decomposed nearly quantitatively to $Co_2[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$. This shows the iodometric determination of $K_3[Fe(CN)_6]$. But if the mixture is kept at room temperature for some hours and an excess of $K_4[Fe(CN)_6]$ is added now, a much smaller quantity of $K_3[Fe(CN)_6]$ is formed, as can be proved by the iodometric determination. This fact leads to the conclusion that, after a longer time, $Co_2[Fe(CN)_6]$ and $Co_3[Fe(CN)_6]_2$ reacted to form a compound, which can not be decomposed completely by an excess of $K_4[Fe(CN)_6]$. In the formation of such a compound the grayish ultramarine blue colour is developed. The analytical results reported in the experimental part indicate that the blue residue, which remains after treatment with $K_4[Fe(CN)_6]$, is $6\,Co_2[Fe(CN)_6]$, $Co_3[Fe(CN)_6]_2$. The formation of the blue compound is prevented if, to the mixture of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$, sodium chloride or potassium chloride is added before the precipitation by the cobalt salt.

Cobalt Prussian blue is also formed if cobalt ferrocyanide, in the presence of an excess of a cobalt salt, is oxidised by small quantities of hydrogen peroxide in acid solution, by nitrous acid and by diluted bromine water.

It was reported by WYROUBOFF[4] that nickel ferrocyanide can also be obtained as a brown substance. However, a brown nickel ferrocyanide has never been observed by another investigator in the seventy-six years which have elapsed since WYROUBOFF's publication. In spite of this fact, REIHLEN AND ZIMMERMANN[5] trusted WYROUBOFF's statement. They tried to explain the existence of a brown and of a light green nickel ferrocyanide by the presence of different anions in these two modifications. This assumption is very improbable. REIHLEN AND ZIMMERMANN themselves did not prepare the brown substance and its existence is doubtful, unless another investigator succeeds in preparing it. Perhaps WYROUBOFF's brown substance was only nickel ferricyanide.

Moreover, WYROUBOFF reports that by precipitation of a nickel salt with ferrocyanic acid he could obtain a dirty green substance $2\ Ni_2[Fe(CN)_6]\cdot Ni_3[Fe(CN)_6]_2 + 47\ H_2O$.

He computed this complicated formula on the basis of a determination of nickel and of iron. In fact, the precipitation of ferrocyanic acid with an excess of a nickel salt or the precipitation of a nickel salt with an excess of ferrocyanic acid leads only to light green nickel ferrocyanide. A substance, the composition of which would be the same or approximately the same as indicated by WYROUBOFF, should necessarily be formed by precipitation of equal volumes of $1/10\ M\ K_4[Fe(CN)_6]$ and $1/10\ M\ K_3[Fe(CN)_6]$ with an excess of a nickel salt. If this is done, precipitation results, the colour of which shows clearly the presence of brown nickel ferricyanide.

In the precipitation of ferrocyanic acid with an excess of a cobalt salt, WYROUBOFF obtained a grayish-green substance of the composition $2\ Co_2[Fe(CN)_6]\cdot Co_3[Fe(CN)_6]_2 + 22\ H_2O$. However, if a cobalt salt is precipitated with an excess of ferrocyanic acid or ferrocyanic acid with an excess of a cobalt salt the green precipitate is cobalt ferrocyanide. As is shown in the experimental part, a substance of the same or approximately the same composition as indicated by WYROUBOFF must be blue. WYROUBOFF could only use the determination of cobalt and of iron to compute the complicated formula. However, MESSNER[6], and later MÜLLER[7] pointed out, that in the group of the iron-cyanogen compounds, if the determinations of the elements are used in computing formulas, this could give very doubtful results. The most important determination, the determination of ferricyan, was not carried out by WYROUBOFF. Therefore, the data mentioned above lead to the conclusion that the ferricyan-ferrocyan compounds of nickel and cobalt ($2\ Ni_2[Fe(CN)_6]\cdot Ni_3[Fe(CN)_6]_2 + 47\ H_2O$ and $2\ Co_2[Fe(CN)_6]\cdot Co_3[Fe(CN)_6]_2 + 22\ H_2O$) described by WYROUBOFF do not exist.

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EXPERIMENTAL

Titrimetric determination of ferricyan in nickel ferricyanide and in cobalt ferricyanide

I. 10 ml 1/10 *M* Ni_2SO_4 were precipitated with 10 ml 1/20 *M* $K_3[Fe(CN)_6]$. Afterwards, 10 ml 1/5 *M* $K_4[Fe(CN)_6]$ and 100 ml H_2O were added. The brown nickel ferricyanide changes into light green nickel ferrocyanide. The latter was filtered, the precipitate washed and in the combined filtrates the ferricyan determined according to MÜLLER AND DIEFENTHAELER[1]. 8.6 ml of a $Na_2S_2O_3$-solution were used up instead of 8.62 ml.

II. Repetition of I. Some ml of a saturated potassium chloride solution were added to the nickel ferrocyanide in order to accelerate the sedimentation. The filtrate required 8.8 ml of a $Na_2S_2O_3$-solution instead of 8.62 ml.

III. 10 ml 1/10 *M* $CoSO_4$ were precipitated with 10 ml 1/20 *M* $K_3[Fe(CN)_6]$. After ten days, 10 ml 1/5 *M* $K_4[Fe(CN)_6]$ were added. The mixture was shaken and diluted with a solution of 10 g potassium chloride in 65 ml water. The green precipitate was filtered and washed with potassium chloride solution. The combined filtrates used up 9.5 ml of a $Na_2S_2O_3$-solution instead of 9.6 ml.

Oxidation of nickel ferrocyanide to nickel ferricyanide by the oxygen of the air in the presence of acids

I. 20 ml 1/10 *M* Ni_2SO_4, 10 ml 1/20 *M* $K_4[Fe(CN)_6]$ and 50 ml diluted hydrochloric acid (2 ml conc. HCl + 48 ml water) were mixed.

II. The same experiment as I. But instead of hydrochloric acid a diluted acetic acid (10 ml glacial acetic acid and 40 ml water) was used.

The samples (I and II) were shaken sometimes. To each of the samples 20 ml water were added after four days, and again 20 ml water after another four days. The mixtures were filtered, the precipitates washed thoroughly with water, and then to each of the precipitates 10 ml 1/5 *M* $K_4[Fe(CN)_6]$ solution was added, whereby light green nickel ferrocyanide was formed. In the filtrates, the potassium ferricyanide was determined. In I 4.92 ml 1/20 *N* $Na_2S_2O_3$, in II 3.5 ml 1/20 *N* $Na_2S_2O_3$ were used up. Therefore, in I were 49.2%, in II were 35% of the ferrocyan oxidised.

III. Was carried out with the same quantities as I. 20 ml water were added after three days and the ferricyan determined after another four days. The filtrate used up 4.98% 1/20 *N* $Na_2S_2O_3$. Therefore, 49.8% of the ferrocyan were oxidised to ferricyan.

IV. Was carried out with the same quantities as II. But instead of hydrochloric acid 50 ml diluted acetic acid (5 ml glacial acetic acid and 45 ml water) were added. The filtrate used up 3.17 ml 1/20 *N* $Na_2S_2O_3$, therefore 31.7% of the ferrocyan were oxidised.

Oxidation of cobalt ferrocyanide to cobalt Prussian blue by the oxygen of the air in the presence of hydrochloric acid

I. 10 ml 1/10 *M* $K_4[Fe(CN)_6]$, 25 ml 1/10 *M* $CoSO_4$ and 10 ml diluted hydrochloric acid (1 ml conc. hydrochloric acid and 9 ml water) and 35 ml water were mixed. 50 ml water were added after four days. The mixture was shaken sometimes. After another three weeks the mixture was filtered and the blue substance washed thoroughly with water containing some $CoSO_4$. The precipitate was washed off into a beaker and 11 ml 1/5 *M* $K_4[Fe(CN)_6]$ were added. Before the filtration some potassium chloride was added. The filtrate used up 1.61 ml 1/10 *N* $Na_2S_2O_3$ solution. Therefore 16% of the ferrocyan were oxidised to ferricyan.

II. 25 ml 1/10 *M* $CoSO_4$, 10 ml 1/10 *M* $K_4[Fe(CN)_6]$, 66 ml diluted hydrochloric acid (0.2 ml conc. hydrochloric acid and 65.8 ml water) were mixed. After four days again 30 ml water were added, and in the same way as I worked up after another eight days. But here, the blue substance was heated to boiling with 15 ml 1/5 *M* $K_4[Fe(CN)_6]$. Later it was cooled down, and some potassium chloride was added. The precipitate was filtered off and washed with potassium chloride solution. The filtrate required 1.61 ml 1/10 *N* $Na_2S_2O_3$. This corresponds to 16% of oxidised ferrocyanide.

III. 25 ml 1/10 *M* $CoCl_2$, 10 ml 1/10 *M* $K_4[Fe(CN)_6]$, 2.5 ml diluted hydrochloric acid (0.5 ml conc. hydrochloric acid and 2 ml water) and 62.5 ml water were mixed and kept at room temperature six days. The Erlenmeyer beaker was shaken sometimes. The precipitate was filtered off and washed with water containing some $CoCl_2$, in order to remove the acid. Later, the blue substance was covered with 10 ml 1/5 *M* $K_4[Fe(CN)_6]$, and sodium chloride was added. The precipitate was again filtered off and washed with a diluted sodium chloride solution. The filtrate used up 1.6 ml 1/10 *M* $Na_2S_2O_3$. This corresponds to 16% of ferricyan formed in this oxidation. The 16% ferricyan found in the experiments I, II and III is only the part of the ferricyan that could be determined because the blue residue also contains ferricyan.

Formation of cobalt Prussian blue by precipitation of mixed solutions of $K_3[Fe(CN)_6]$ *and* $K_4[Fe(CN)_6]$ *with a cobalt salt*

The following table shows that even if ferrocyan and ferricyan are changed within wide limits blue substances still result.

In all precipitations (1 to 4) the mixtures were diluted to 50 ml with water, kept at room temperature some days and shaken sometimes. However, 3 ml 1/10 *M* $K_3[Fe(CN)_6]$, 1 ml 1/10 *M* $K_4[Fe(CN)_6]$, 9 ml 1/10 *M* $CoCl_2$ (instead of the calculated 6.5 ml) and 37 ml water give a violet precipitation.

References p. 324.

	ml 0.1 M				
	$K_4[Fe(CN)_6]$	$K_3[Fe(CN)_6]$	$CoCl_2$	$CoCl_2$ calculated	mol ratio of $Co_2[Fe(CN)_6]$ and $Co_3[Fe(CN)_6]_2$
1	6	1	15	13.5	12 $Co_2[Fe(CN)_6]$: $Co_3[Fe(CN)_6]_2$
2	5	1	13	11.5	12 $Co_2[Fe(CN)_6]$:6/5$Co_3[Fe(CN)_6]_2$
3	2.5	2.5	11	8.75	12 $Co_2[Fe(CN)_6]$: 6 $Co_3[Fe(CN)_6]_2$
4	2	3	11	8.5	12 $Co_2[Fe(CN)_6]$: 9 $Co_3[Fe(CN)_6]_2$

I. 4.8 ml 1/10 M $K_3[Fe(CN)_6]$, 5 ml 1/10 M $K_4[Fe(CN)_6]$, 20.5 ml 1/10 M $CoCl_2$ and 50 ml water were mixed. Immediately afterwards 10 ml 1/5 M $K_4[Fe(CN)_6]$ were added. One hour later 10 g sodium chloride were added and the mixture was shaken. The precipitation was filtered and washed with sodium chloride solution. The filtrate required 4.7 1/10 N $Na_2S_2O_3$ instead of 4.8 1/10 N $Na_2S_2O_3$.

II. 2 ml 1/5 M $K_4[Fe(CN)_6]$, 10 ml 1/20 M $K_3[Fe(CN)_6]$, 20 ml 1/10 M $CoSO_4$ were mixed. Immediately afterwards 10 ml 1/5 M $K_4[Fe(CN)_6]$ were added, and then 10 g potassium chloride. The mixture was diluted with water to 80 ml and kept over night. On the next day the precipitate was filtered off and washed with potassium chloride solution. The filtrate required 9.36 ml 1/20 N $Na_2S_2O_3$ instead of 10 ml 1/20 N $Na_2S_2O_3$.

Experiments I and II demonstrate that immediately after the precipitation cobalt ferrocyanide and cobalt ferricyanide are not yet combined.

III. 10 ml 1/20 M $K_4[Fe(CN)_6]$, 10 ml 1/20 M $K_3[Fe(CN)_6]$, 20 ml 1/10 M $CoSO_4$ and 35 ml water were mixed. After four days the cobalt solution was decanted from the precipitate through a filter. To the precipitate were added 15 ml 1/5 M $K_4[Fe(CN)_6]$. On the next day potassium chloride was added. The blue precipitate was filtered and washed with potassium chloride. The filtrate required 6.45 ml 1/20 N $Na_2S_2O_3$. Therefore 3.55 ml, *i.e.* about one third of the ferricyanide which was used in this experiment was retained in the formation of the cobalt ferrocyan-ferricyan compound.

IV. The quantities were the same as in III. The mixture was kept at room temperature for 8 days. After the addition of 15 ml 1/5 M $K_4[Fe(CN)_6]$ the mixture was kept in a boiling water bath for some minutes. Later it was cooled down, 15 ml water and some potassium chloride was added. The precipitate was filtered and washed with potassium chloride solution. The filtrate required 6.45 ml 1/20 N $Na_2S_2O_3$ as in III.

V. The same quantities as in I. After three days the cobalt solution was decanted through a filter. To the precipitate 10 ml 1/5 M $K_4[Fe(CN)_6]$ were added and afterwards 10 g sodium chloride. The precipitate was filtered and washed with sodium chloride solution. The filtrate used up 3.4 ml 1/10 N $Na_2S_2O_3$. Therefore 1.6 ml 1/10 M $K_3[Fe(CN)_6]$ *i.e.*, one third of the potassium ferricyanide was used up in the formation of the cobalt ferrocyan-ferricyan compound.

VI. This experiment was carried out with the same quantities as V. After ten days 10 ml 1/5 *M* $K_4[Fe(CN)_6]$ were added. The mixture was heated to boiling. The other procedure was the same as in V. The filtrate required 3.5 ml 1/10 *N* thiosulphate.

The results in the experiments III, IV, V and VI show that the blue residue obtained after the treatment with potassium ferrocyanide is 6 $Co_2[Fe(CN)_6]\cdot Co_3[Fe(CN)_6]_2$.

VII. The same quantities as in I. However, here 11 g sodium chloride were given to the potassium ferricyanide-potassium ferrocyanide mixture before the precipitation with $CoSO_4$. The mixture was diluted to 80 ml. After four days the precipitate was here more violet and less blue than in III, IV, V and VI. 10 ml 1/5 *M* potassium ferrocyanide were added, and later 10 g sodium chloride. The filtrate required 4.6 ml 1/10 *N* $Na_2S_2O_3$ instead of 4.8 ml $Na_2S_2O_3$.

VIII. 11 ml 1/10 *M* $CoSO_4$ were mixed with 10 ml 1/20 *M* potassium ferrocyanide, 30 g potassium chloride added and with water diluted to 110 ml. On the next day 9 ml 1/10 *M* $CoSO_4$ and 9.6 ml 1/20 *M* potassium ferricyanide were added. After another six days the solution was decanted through a filter and to the precipitate which was retained in the Erlenmeyer beaker 10 ml 1/5 *M* $K_4[Fe(CN)_6]$ were added. The precipitate was filtered through the filter that was used for decanting and washed with potassium chloride solution. The filtrate required 9 ml 1/20 *N* $Na_2S_2O_3$ instead of 9.6 ml $Na_2S_2O_3$. Experiments VII and VIII disclose that the addition of sodium chloride or potassium chloride prevents the formation of cobalt Prussian blue .

Precipitation of nickel solutions and of cobalt solutions with ferrocyanic acid

I. Excess of nickel chloride: 5 ml 1/10 *M* potassium ferrocyanide and 20 ml 1/10 *N* hydrochloric acid were mixed with 12 ml 1/10 *M* nickel chloride. A light green precipitate of nickel ferrocyanide was formed. On the next day, the colour of the precipitate was already slightly yellow, but the addition of alkali produced light green nickel (II) hydroxide.

II. Excess of ferrocyanic acid: 5 ml 1/10 *M* potassium ferrocyanide, 20 ml 1/10 *N* hydrochloric acid and 5 ml 1/10 *M* nickel chloride were mixed. The precipitate was here light bluish green, but on the next day the colour turned into light green. Addition of alkali produced light green nickel (II) hydroxide.

III. Excess of cobalt chloride: 40 ml 1/10 *N* hydrochloric acid, 10 ml 1/10 *M* potassium ferrocyanide and 22 ml 1/10 *M* cobalt chloride were mixed. Cobalt ferrocyanide of the characteristic green colour was obtained. On the next day, the colour turned into grayish green and later into bluish green.

IV. Excess of ferrocyanic acid: 15 ml 1/10 *M* potassium ferrocyanide, 60 ml 1/10 *N* hydrochloric acid and 10 ml 1/10 *M* cobalt chloride were mixed. The originally slimy precipitate turned into a grayish green sediment.

SUMMARY

Nickel ferrocyanide in presence of acids is oxidised by the oxygen of the air to nickel ferricyanide. Cobalt ferrocyanide is oxidised under the same conditions to a ultramarine blue substance with a slight grayish tinge. This substance is very similar to Prussian blue and to Turnbull's blue and could be called cobalt Prussian blue. This blue substance is also formed if mixtures of potassium ferrocyanide and potassium ferricyanide are precipitated with an excess of cobalt salt. This investigation led to the conclusion that the blue substance is probably not a mere mixture of cobalt ferrocyanide and cobalt ferricyanide, but the compound $6\ Co_2[Fe(CN)_6].Co_3[Fe(CN)_6]_2$. A new method of the determination of ferricyan is described. Moreover, it was proved that some statements of former investigators on the reactions of nickel and cobalt with iron-cyanogen compounds are erroneous, and some iron-cyanogen compounds of nickel and cobalt described in the literature do not exist at all.

RÉSUMÉ

Le ferrocyanure de nickel, en présence d'acides, est oxydé par l'oxygène de l'air en ferricyanure de nickel. Le ferrocyanure de cobalt est oxydé, dans les mêmes conditions, en un composé bleu outremer légèrement grisâtre. Ce corps est très semblable au bleu de Prusse et au bleu de Turnbull, on pourrait l'appeler ,,bleu de Prusse cobaltique''. Ce composé bleu se forme aussi si l'on précipite un mélange de ferro- et ferricyanure de potassium avec un sel de cobalt en excès. On arrive à la conclusion que cette substance bleue n'est probablement pas un mélange de ferro- et ferricyanure de cobalt, mais le composé: $6\ Co_2[Fe(CN)_6].Co_3[Fe(CN)_6]_2$. Une nouvelle méthode de dosage des ferricyanures est décrite. D'autre part, il a été démontré que les hypothèses de certains auteurs sur les réactions du nickel et du cobalt avec les composés ferro- et ferricyanés sont fausses, et certains composés décrits dans la littérature n'existent pas.

ZUSAMMENFASSUNG

Das Nickelferrocyanid oxydiert sich in Gegenwart von Säuren durch den Luftsauerstoff zum Nickelferricyanid. Das Kobaltferrocyanid oxydiert sich unter den gleichen Bedingungen zu einer schwach graustichig ultramarinblauen Substanz. Diese Substanz ist dem Berlinerblau und auch dem Turnbullsblau sehr ähnlich und kann Kobaltberlinerblau genannt werden. Diese blaue Substanz entsteht auch, wenn man Mischungen von Ferrocyankalium und Ferricyankalium mit überschüssigem Kobaltsalz fällt und nachher einige Tage unter Umschütteln stehen lässt. Diese Untersuchung hat zu dem Schlusse geführt, dass das Kobaltberlinerblau wahrscheinlich nicht eine blosse Mischung von Kobaltferrocyanid und Kobaltferricyanid ist, sondern die chemische Verbindung $6\ Co_2[Fe(CN)_6] \cdot Co_3[Fe(CN)_6]_2$ darstellt. Es wird eine neue Methode zur Bestimmung des Ferricyans im Nickelferricyanid und im Kobaltferricyanid angegeben. Diese Methode wurde in dieser Arbeit benützt. Ferner ist erwiesen worden, dass mehrere Angaben früherer Autoren über die Reaktionen des Nickels und des Kobalts mit den Eisencyanverbindungen irrig sind und dass einige in der Literatur beschriebene Eisencyanverbindungen des Nickels und Kobalts überhaupt nicht existieren.

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QUALITATIVE AND QUANTITATIVE ANALYSIS OF MIXTURES OF SULFONAMIDES V.

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CHROMATOGRAPHIC METHODS

In the previous communications the qualitative analysis of mixtures of sulfonamides was treated in a "classical" manner, namely by making use of a variety of solvents. In this way, it has not always been possible to achieve a complete separation and identification; moreover, the methods described were often lengthy and required a relatively large quantity of material. To overcome these difficulties, chromatographic methods are of great value. We therefore investigated them in a general way, not restricting ourselves to a small number of mixtures of known composition. However, there is a close connection with the general "classical" scheme treated in the previous communications, as will be seen below.

A number of papers concerning the chromatography of mixtures of sulfonamides is found in the literature. LONGENECKER[64] described the separation of sulfadiazine, sulfamerazine and sulfamezathine by means of *n*-butyl alcohol and ammonia. His technique has been used in a part of our investigation, and will be discussed below. THOMAS, RANSY, ROLAND AND VANDEN BULCKE[65] described in detail the qualitative and quantitative analysis of two mixtures, *viz.* sulfadiazine, sulfamerazine with sulfamezathine, and sulfadiazine, sulfamerazine with sulfathiazole. Furthermore, chromatographic investigations have been published by HEINÄNEN, NYYSSÖNEN AND TUDERMAN[66], TAKAGI, SUZUKI AND IMAEDA[67], ROBINSON[68], WANKMÜLLER[73], JAKUBEC[74] and by SAM AND ULTÉE[75].

The following techniques were used in our investigations.

1. Ascending paper chromatography with strips of filter-paper (Whatman No. 2) of 23.5 × 6.5 cm. A pencil-line was drawn parallel to the narrow side of the paper, at a distance of 2.5 cm from the underside. The samples to be tested were dissolved in acetone or water (conc.: 0.2-0.5%). Small droplets of these solutions were placed on the pencil-line by means of a capillary-pipette.

The solvent of each drop was evaporated from the paper before a new droplet was spotted at the same place, to avoid too great an extension of the area occupied by the dissolved sample. The diameter of each spot did not exceed 3 mm.

Three drops of a solution of 0.3% sufficed for an analysis. On each strip of filter-paper, three different solutions were spotted at regular intervals.

The strip was placed in an air-tight cylinder containing the developer in a small vessel. The paper ranged into this vessel and was fixed to the top of the cylinder in such a way that it did not touch the wall of the container.

Elution was continued until the front of the liquid had attained a distance of a few cm from the top of the paper. This was then removed from the cylinder, the position of the front marked with a pencil and the paper dried. Next, the spots were made visible by spraying with a suitable reagent (see below).

2. Ascending paper chromatography with very narrow strips of filter-paper: 23.5 × 0.4 cm. Each strip was used for one solution only. The method was the same as described above.

These narrow strips were already applied by LONGENECKER[64]; they indeed proved to have advantages over the broader ones: the separation of the different bands was usually better and they were smaller and sharper limited than the spots on the broader strips. Furthermore, already one small drop of a 0.3% solution sufficed for an analysis.

3. Two-dimensional paper chromatography. Filter-paper of size 23.5 × 23.5 cm was used. Drops of the solution to be analyzed were placed in one of the angles of the paper (but not too close to the sides), which after this was rolled into a cylinder. Two opposite sides were clipped with paper-clips. The whole (Fig. 22) was placed in the cylinder containing the vessel with the first elution-liquid. Elution was continued as long as possible; after drying the paper it was again rolled into a cylinder, but now with the axis perpendicular to the one of the first cylinder (Fig. 22: A and B). Hereafter the second developer was used. After drying again, the paper was sprayed with the reagent.

On applying this technique of "rolling-up" the square paper, no large trough is required for the development of the chromatogram. The same cylinder can be used as mentioned under 1 and 2.

Since the sulfonamides are colourless substances, a suitable reagent had to be used to make the spots of the compounds visible. For this a reaction was needed which exhibited the following properties (*cf.* RUTTER[69]):

sensitive;

reproducible;

holding for all compounds taken into consideration;

easy to apply.

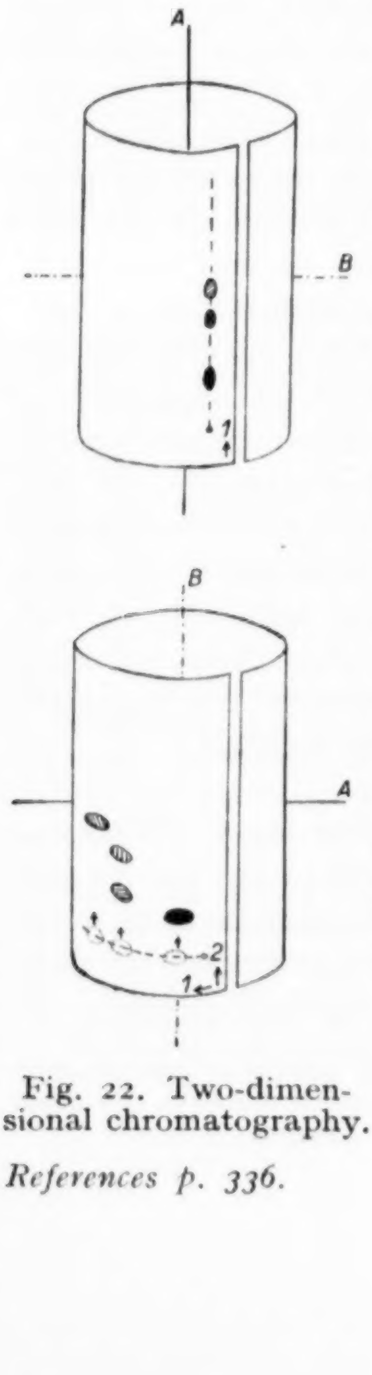

Fig. 22. Two-dimensional chromatography.

A number of reactions which seemed to be suitable were studied: silver-salts, mercury salts, salts of copper, cobalt and nickel, formaldehyde with silver nitrate, furfurol and acetic acid, *p*-dimethylaminobenzaldehyde (Ehrlich's reagent). Only the last two reactions proved to be of general applicability but of these two the one with Ehrlich's reagent was by far the most sensitive, and therefore used in our investigations.

The reagent was prepared by dissolving 0.5 g of *p*-dimethylaminobenzaldehyde in 5 ml of 2 *N* hydrochloric acid, and adding water to 250 ml. With this reagent, 0.5 γ sulfonamide could just be made visible. If higher sensitivity was desired, a reagent solution was employed which was five times as concentrated as the above one. The application of the solution was very simple: it was sprayed over the previously dried paper by means of an atomizer; the spots of the sulfonamides were at once coloured yellow. The intensity of the colour depended on the concentrations of the compound, of course.

The reagent has only one drawback: it only reacts with sulfa's containing a free aromatic amino-group. Succinylsulfathiazole and septazine yield a yellow colour only in so high a concentration as will never be met in practice. We could not overcome this difficulty, unfortunately. In this part of our investigations, therefore, these two compounds could not be taken into account.

We did not apply the irradiation of the paper with ultraviolet light, since the *p*-dimethylaminobenzaldehyde reaction proved to be quite sufficient for our purpose; moreover, previous to the irradiation, the paper needs a treatment with HCl-vapour during 5 hours in vacuum. This makes the application rather tedious.

The nature of the unknowns in the mixture can be determined from the positions of the various spots on the chromatograms in different manners. We mention:

a. Determination of the R_F value, which is defined as the ratio

$$\frac{\text{distance covered by the compound}}{\text{distance covered by the front of the liquid}}$$

b. Determination of the R_G value:

$$\frac{\text{distance covered by the unknown}}{\text{distance covered by a known substance under the same circumstances}}$$

c. The chromatogram in question is compared with another one, run at the same time and in the same way, and made from a mixture of the sulfonamides that are supposed to be present in the original sample. Conclusions about this presence can be drawn from the R_F or R_G values.

d. The mixture to be examined is run for a second time after addition of the compounds present. The number of spots in this second chromatogram then must be the same as in the first one, if the suppositions about the nature of the unknowns have been correct.

The first two methods are very easy to perform, but the results have to be handled with some care. The R_F (R_G) value of a compound, namely, is not a constant, but depends upon a number of external conditions: the nature of the filter-paper, the quantity of substance present, the temperature, the form of the filter-paper, etc. The last effect appeared very clearly in the differences between the R_F values of the broad and the narrow filter-papers (see below).

Furthermore, the R_F value is highly dependent upon the pH of the developing liquid. This effect presumably appears if compounds with dissociable groups are chromatographed (for examples we refer to GORDON[70], LANDUA, FUERST AND AWAPARA[71]). Since the sulfa's also contain ionizable groups, this effect was obviously met with here. For that reason there was no sense in measuring the R_F very exactly, since our developers were not buffered at a definite pH.

For all these reasons we supposed it better to lay stress on the comparison with known compounds in identifying the spots of a paper-chromatogram. The R_F values listed below must be regarded as an orientation, therefore.

The analysis of a mixture now proceeded as follows.

At first, the dried and pulverized mixture was divided into a water-soluble and a water-insoluble part. The technique has already been described in our second communication, but was performed here on a microchemical scale, of course. Centrifuge cones were used for the separation of the solution and the insoluble part. After centrifuging the clear solution was removed by means of a micro-pipette and transferred to another centrifuge cone. The residue was washed with water. In this way there was obtained:

a clear solution containing the water-soluble sulfonamides . . . . Group I
a residue containing the water-insoluble sulfonamides . . . . Group II

Treatment of Group I

For a survey of the compounds present in this group, and of the possibilities of further separation, we may refer to our second communication.

Here we could choose between two methods:

a. A further separation might be accomplished with dilute acetic acid.

b. A few test-chromatograms might first be made to get an impression of the composition of the mixture. If necessary, further separation into sub-groups might be performed after this.

The last way seemed to be the best one. By regrettable circumstances the following compounds of group I were not at our disposal at the time of this part of the investigation: sulfacetamide, sodium sulfacetamide and soluseptazine. Data of these compounds cannot be given here, therefore.

For a test-chromatogram, a 0.5-1% aqueous solution of the compounds of

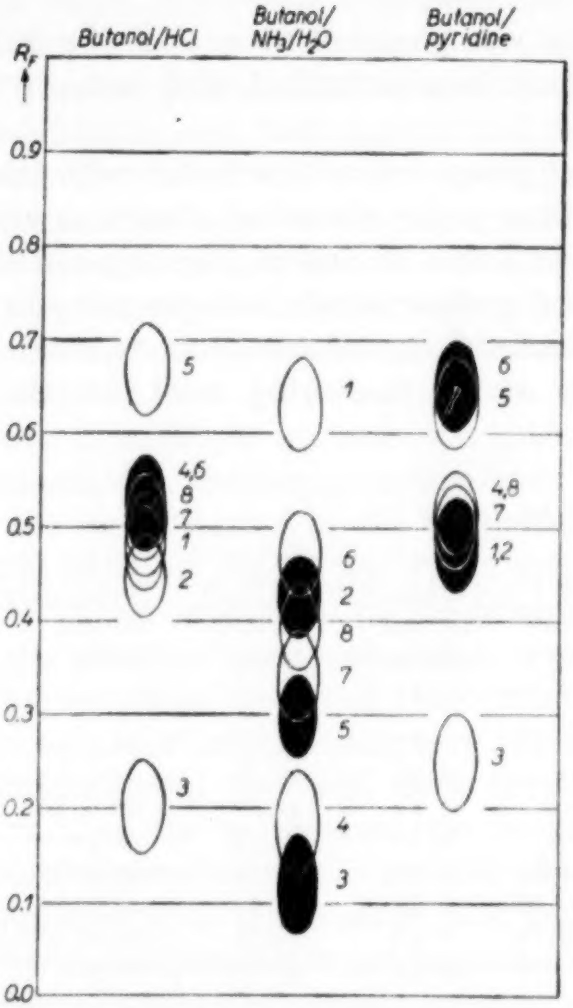

Fig. 23. Analysis of Group I. Filter-paper 23.5 × 6.5 cm.

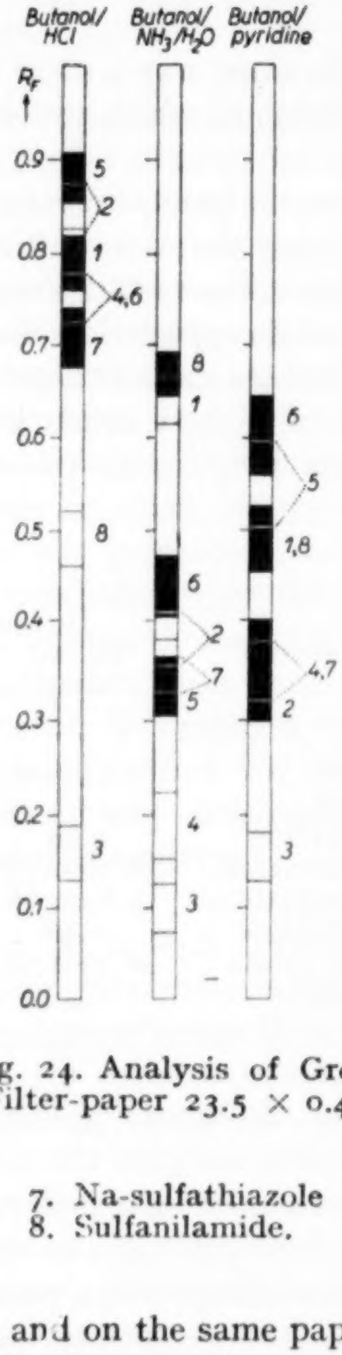

Fig. 24. Analysis of Group I. Filter-paper 23.5 × 0.4 cm.

Meaning of the figures:

1. Na-irgafen
2. Na-irgamid
3. Na-sulfadiazine
4. Na-sulfamerazine
5. Na-sulfamezathine
6. Na-sulfapyridine
7. Na-sulfathiazole
8. Sulfanilamide.

group I was prepared. Together with this solution and on the same paper, a few standard solutions of known composition were run. In these solutions each sodium salt was present at a concentration of a 0.5%.

A large number of various solvents were tested as elution liquids. Finally, the following three ones were selected.

1. 40 ml of *n*-butyl alcohol (distilled, b.p. 116-118°) were added to 10 ml of concentrated ammonia (25%) and distilled water added to 100 ml. The liquid (consisting of two layers) was vigorously shaken and set aside for some hours, with occasional shaking. The alcoholic layer was then decanted and used as developer. This solution will hereafter be called "butanol/NH_3/H_2O".

2. 5 ml of dilute HCl (1:10) were added to 50 ml of *n*-butyl alcohol. After

well shaking a clear solution resulted, which was used for the elution ("butanol/HCl").

3. In the same way a clear solution was prepared from 5 ml of pyridine and 40 ml *n*-butanol, which previously had been saturated with water ("butanol/pyridine").

Different mixtures of compounds of group I were now tested with these three solvents, using the narrow strips of filter-paper (described above) as well as the broader ones. The results are given in Table VI and in Figs. 23 and 24. Since the compounds appeared in the form of spots or bands, it is necessary to indicate the part of these spots or bands to which the R_F value relates. As usual, we took the point of highest colour-intensity as the measuring point for the R_F (*cf.* CONSDEN *et al.*[72], LANDUA *et al.*[71].

TABLE VI

Compound	Butanol/HCl Broad strip	Butanol/HCl Narrow strip	Butanol/NH_3/H_2O Broad strip	Butanol/NH_3/H_2O Narrow strip	Butanol/pyridine Broad strip	Butanol/pyridine Narrow strip
Na-irgafen	0.45-0.50	0.72-0.78	0.67	0.69	0.45-0.53	0.50
Na-irgamid	0.40-0.45	0.85	0.40	0.46	0.45-0.53	0.30-0.40
Na-sulfadiazine	0.20	0.20	0.13	0.10	0.20-0.30	0.17
Na-sulfamerazine	0.50-0.55	0.75	0.20	0.15	0.50	0.35
Na-sulfamezathine	0.63-0.66	0.80-0.90	0.30	0.34	0.60-0.67	0.50-0.60
Na-sulfathiazole	0.48	0.65-0.75	0.34	0.34	0.45-0.55	0.36
Na-sulfapyridine	0.53-0.58	0.65-0.72	0.48	0.58	0.60-0.70	0.68
Sulfanilamide	0.49	0.45-0.50	0.37	0.65	0.50	0.47

However, the figures of Table VI do not give an impression of the forms of the various spots, nor give the schemes in Figs. 23 and 24. Since photographic reproduction of the light-yellow spots is very difficult, we can only give a short verbatim description of the chromatograms. It appeared that butanol/NH_3/H_2O was the most prominent developer if the broad strips were used. In this case the spots were finer, sharper and smaller, and very well separated. In using butanol/pyridine the spots were rather irregular, large and unsharp. The narrow strips of filter-paper gave better results with butanol/HCl and butanol/pyridine, but in this case also the bands were somewhat broader and less well separated than with butanol/NH_3/H_2O. If a mixture was analyzed on both the broad and the narrow strips, the latter always showed a much better separation of the components than the former, especially when butanol/pyridine was used. In the bands, the most intensely coloured parts were usually sharper and of smaller surface than in the spots, which resulted in a better separation (with identical R_F in both cases).

It is highly remarkable that sometimes the R_F of a compound chromatographed on the narrow strips had a value completely different from the one on the broad strips. Numerous examples may be found in Table VI.

We shall now return to our problem.

A few chromatograms of the mixture to be tested were made, using different developing liquids, and both narrow and broad strips of filter-paper. The compounds were then identified by determining the R_F values of the different spots. The further method depended on the result of this first examination.

If the number of components was small and their identity readily established, the analysis was repeated, either with a mixture prepared from the pure components or with the original sample, but now after the addition of a small quantity of each of the pure compounds. In this way, the nature of the components of a simple mixture was always established without difficulty.

If, however, the number of components was not so small, or if difficulties arose in the identification of the components (by the presence of compounds with nearly identical R_F values, which might be concluded from the shape of the spots), further separation of the mixture was necessary. For this, we may refer to the previous communications, which dealt with these separations in detail. The technique described there must somewhat be modified, of course, since here we are often handling very small samples. We shall not discuss the microtechniques used, however, since they were in no way different from the ones described in the well-known text-books on microchemistry.

We wish to draw attention to the following details.

The separation with dilute acetic acid transforms the sodium salts (group I!) into the "free" compounds; in subsequent chromatographic analysis the mixture must therefore be regarded as containing only compounds of group II (see below). The dilute acetic acid solution must be evaporated to dryness previous to the further analysis, in order to remove the acid as completely as possible. If present, it causes troublesome tailing of the spots.

On further separation with ethyl alcohol it must be borne in mind that this separation is not a quantitative one, especially not in group Ia. The presence, in some group, of small quantities of compounds belonging to another one seldom interferes in the classical scheme, but is at once detected with chromatographic methods. To avoid this difficulty it is better to choose other separations. We give the following example. In group II, irgafen is isolated via its slightly soluble sodium salt; after filtration, irgamid is precipitated with dilute hydrochloric acid (*cf.* our fourth communication). Here, however, it would be uneconomical to apply two separations, since one suffices. Irgafen and irgamid both precipitate in dilute hydrochloric acid, and are well separated in the chromatograms; therefore, they can safely be taken together in one group. For this purpose, the precipitation (obtained after addition of acetic acid, *cf.* the second paper) is dissolved in NaOH (4%). HCl (1%) is then added *very carefully and drop by drop* to the clear solution. A precipitation occurs at the neutral point;

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the addition of HCl is continued *after* the precipitation has been settled (to avoid serious retardation of crystallization).

The precipitation is centrifuged, washed with dilute HCl, dried and redissolved in water with slight heating. The free compounds are then precipitated with dilute NaOH. This must be done since the hydrochlorides show a strong effect of tailing in the chromatogram, while the free compounds do not.

The sulfonamides remaining in the acid solution after separation of irgafen and irgamid are likewise isolated as the free compounds by adding NaOH, and chromatographed without any further treatment. If now there are still indications of the presence of more compounds in one spot or band, two-dimensional chromatography may be applied. This technique may also be used, of course, before application of the various separations mentioned, either to avoid them or merely as an orientation. This two-dimensional chromatography will be discussed below.

TABLE VII

Compound	Butanol/HCl Broad strip	Butanol/HCl Narrow strip	Butanol/NH_3/H_2O Broad strip	Butanol/NH_3/H_2O Narrow strip	Butanol/pyridine Broad strip	Butanol/pyridine Narrow strip
Sulfanilamide	0.49	0.46	0.37	0.66	0.55	0.51
Irgafen	0.78	0.80	0.54	0.71	0.49	0.45-0.47
Sulfaguanidine	0.26	0.30	0.34	0.52	0.30	0.35
Irgamid	0.69	0.85	0.30	0.48	0.50	0.50-0.53
Sulfadiazine	0.60-0.65	0.72	0.11	0.21	0.24	0.26
Sulfamerazine	0.60-0.63	0.68-0.73	0.19	0.29	0.42-0.46	0.35-0.40
Sulfamezathine	0.90	0.70-0.80	0.34	0.49	0.65	0.55-0.60
Elkosin	0.60	0.73-0.78	0.34	0.43-0.46	0.40-0.44	0.35
Sulfapyridine	0.55-0.60	0.65-0.70	0.39	0.27	0.65	0.63
Sulfathiazole	0.59	0.67-0.70	0.28	0.40-0.42	0.47	0.32-0.35
Sulfamethylthiazole	0.70-0.75	0.75-0.80	0.41	0.58-0.65	0.65	0.60-0.65

Treatment of Group II

The search was conducted as described in group I. The water-insoluble mixture was dried and dissolved in acetone (concentration nearly 0.5%). Next, a number of chromatograms were made on both narrow and broad strips of filter-paper and with various solvents. The different possibilities are listed in Table VII and Figs. 25 and 26. In contrast with the results of group I, butanol/pyridine appeared to be an excellent developer here, as well as butanol/NH_3/H_2O; both solvents were excellently complementary to one another. As examples we mention:

sulfamezathine, elkosin and sulfaguadine	no separation by butanol/NH_3/H_2O, but an excellent separation by butanol/pyridine;
sulfamerazine and elkosin	separation by butanol/NH_3/H_2O, no separation by butanol/pyridine.

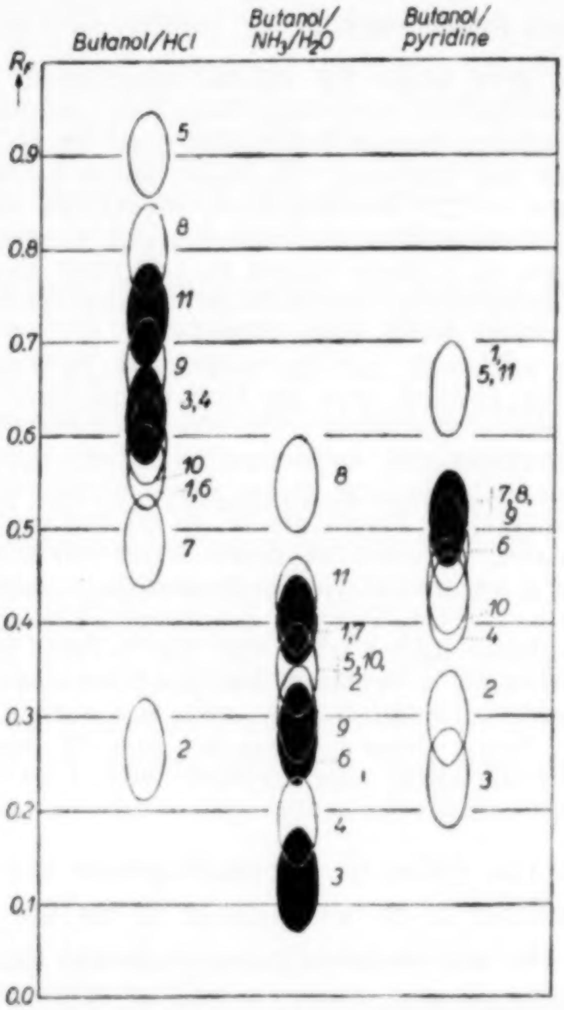

Fig. 25. Analysis of Group II.
Filter-paper 23.5 × 6.5 cm.

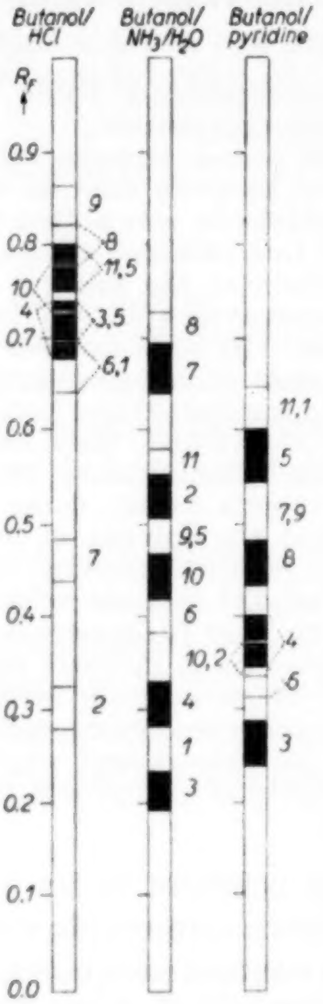

Fig. 26. Analysis of Group II.
Filter-paper 23.5 × 0.4 cm.

Meaning of the figures:

1. Sulfapyridine
2. Sulfaguaninidine
3. Sulfadiazine
4. Sulfamerazine
5. Sulfamezathine
6. Sulfathiazole
7. Sulfanilamide
8. Irgafen
9. Irgamid
10. Elkosin
11. Sulfamethylthiazole.

TABLE VIII

Compound	ROBINSON[68] Butanol/ NH$_4$OH	ROBINSON[68] Butanol/ Acetic Acid	LONGENECKER[64] Butanol/NH$_3$/H$_2$O	JAKUBEC[74] Butanol/ Diethyl-amine	JAKUBEC[74] Butanol/ Acetic Acid
Sulfaguanidine	0.43	0.36		0.40	0.45
Sulfathiazole	0.48	0.46	0.38	0.58	0.76
Sulfanilamide	0.56	0.42		0.50	0.54
Sulfadiazine	0.24	0.50	0.17	0.28	0.79
Sulfamezathine	0.48	0.48		0.69	0.86
Sulfamerazine	0.34	0.50	0.30		
Sulfacetamide	0.71	0.44		0.23	0.79
Sulfapyridine	0.70	0.51		0.74	0.79

Butanol/HCl yielded diffuse spots and broader bands, and as a developer was therefore less suitable than the two other ones.

In the accompanying Table VIII we give some R_F values mentioned in the literature, for comparison.

It must be noted, however, that the solvent butanol/NH_4OH used by ROBINSON was prepared in quite another way than our butanol/NH_3/H_2O, since *p*-dimethylaminobenzaldehyde was added to it prior to the development. Moreover the spots on the base-line of the filter-paper strips were sprayed with Ehrlich's reagent before application of the solvent. Therefore, it is more exact to say that ROBINSON analysed chromatographically the *p*-dimethylaminobenzaldehyde compounds of the sulfonamides. His data cannot be compared with ours, therefore.

The three data of LONGENECKER agree well with our R_F values for butanol/NH_3/H_2O and the narrow strips. LONGENECKER, indeed, was the first to use these strips. As already mentioned, they have certain advantages over the broader ones.

Diethylamine/butanol, used by JAKUBEC, proved to be an excellent developing liquid. JAKUBEC's paper came only recently to our knowledge, however, so we could not use the solvent in our investigation. Preparation: 90 ml butanol, 10 ml ethanol, 0.1 ml diethylamine, 97 ml water; is used 24 hours after mixing.

THOMAS *et al.*[65] did not record the R_F values of the compounds investigated. They used circular filter-papers and butanol/NH_3/H_2O as a solvent. The sequence of the various rings in their chromatograms agree with the R_F values listed in Table VII. These authors further mentioned a method for the identification of the spots or rings *viz.* by observing the colours yielded after spraying with Ehrlich's reagent in ultraviolet and visible light. Since these colours are largely dependent on the quantity of compound present in the spot, this method cannot be called a reliable one.

From the positions of the spots on the different chromatograms the nature of the unknown compounds was determined as far as possible. If further separations in the mixture were necessary (*cf.* the treatment of group I above) the group-separations discussed in our fourth communication were followed. These are not quantitative, of course, but in every group the quantity of interfering admixture is very small. The following points proved to be of importance, however:

1. the solubility of irgafen in NaOH;
2. the solubility of irgamid in HCl;
3. the solubility of some compounds of group IIb in boiling water.

The last difficulty could be evaded by recrystallizing group IIa once more from a small quantity of boiling water (filtration at the boiling temperature).

Both of the other difficulties could hardly be evaded. The two compounds are so slightly soluble, however, that, by the use of a 0.1% solution of the mixture, the quantity of irgafen or irgamid present could hardly be detected by the *p*-dimethylaminobenzaldehyde reagent. Very important conclusions could be drawn, therefore, from the change in intensity of the various spots before and after the group separations.

This principle, of course, can also be applied to the treatment of group I described above.

Another solution for the difficulties was the application of two-dimensional chromatography. The technique has already been described above. The only

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solvents that could be used here were butanol/pyridine and butanol/NH_3/H_2O. Butanol/HCl caused too diffuse spots.

The method was tried with five mixtures, compounded resp. of
sulfadiazine, sulfamerazine and sulfathiazole;
sulfadiazine, sulfamerazine, sulfamezathine and elkosin;
irgafen, irgamid and sulfaguanidine;
sulfadiazine, sulfamerazine, sulfamezathine and sulfanilamide;
sulfadiazine, sulfamerazine, sulfamezathine and sulfathiazole.

These mixtures were first developed with butanol/pyridine and next with butanol/NH_3/H_2O. The various R_F values agreed very well with those previously found in one-dimensional chromatography. The separation of the spots was always very good, though their area was somewhat larger and more diffuse, of course, than in the one-dimensional chromatography.

Summarizing, we may say that also in the analysis of mixtures of sulfonamides chromatographic analysis has proved to be a valuable tool. It can be used either as an individual method or as an expedient for the classical separation scheme, which was amply discussed in our previous communications. Both methods enable the qualitative analysis of all mixtures of sulfonamides occurring in practice.

The next papers will deal with various methods for the quantitative determination of the components of these mixtures.

SUMMARY

Various methods are described for the chromatographic analysis of mixtures of sulfonamides. The division into a water-soluble and a water-insoluble group, which formed the base of the "classical" separation scheme (treated in the previous communications), was also used here. The R_F values are listed in Table VI and VII. In one-dimensional chromatography, both narrow and broad strips of filter-paper were used; sometimes, a very marked difference between the R_F values of a compound on both kinds of strips was noted. Schemes of the results are given in Figs. 23, 24, 25 and 26. Two-dimensional chromatography was also applied.

RÉSUMÉ

On décrit quelques méthodes d'analyse chromatographique de mélanges de sulfamidés. La séparation en groupes de sulfamidés solubles et insolubles dans l'eau, (formant la base de la méthode „classique" décrite dans les mémoires précédents), est employée aussi ici. Les valeurs R_F sont mentionnées dans les Tableaux VI et VII. Dans le chromatographie à une dimension on emploie des bandes de papier filtre étroites et larges; quelquefois on constate une différence très remarquable entre les valeurs R_F d'un composé sur ces deux sortes de bandes. Les schémas des résultats sont donnés dans les Figs. 23, 24, 25 et 26. On a employé aussi la chromatographie à deux dimensions.

ZUSAMMENFASSUNG

Verschiedene Methoden werden beschrieben für die chromatographische Analyse von Sulfonamidgemengen. Die Trennung in eine wasserlösliche und eine wasser-

unlösliche Gruppe, welche die Basis des in den vorigen Mitteilungen besprochenen „klassischen" Schemas bildete, wurde auch hier angewandt. Die R_F Werte sind in Tabelle VI und VII angeführt. In der eindimensionalen Chromatographie wurden schmale und breite Streifen Filtrierpapier gebraucht; manchmal wurden sehr auffallende Unterschiede beobachtet zwischen den R_F Werten einer Verbindung auf beiden Streifensorten. Schemas der Resultate sind in den Figuren 23, 24, 25 und 26 gegeben. Die zweidimensionale Chromatographie wurde ebenfalls angewendet.

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ALKALIMETRIC METHOD FOR THE ESTIMATION OF CADMIUM AND ZINC, IN CADMIUM-COPPER AND ZINC-COPPER ALLOYS

by

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The method for the estimation of cadmium and zinc using potassium iodide[1] and sodium thiosulphate[2] as reagents has been extended for the estimation of the same in copper-containing mixtures.

Sodium hydrogen carbonate, used as the precipitant in the above method, keeps copper(II) in solution, allowing complete separation of cadmium and zinc from copper-containing mixtures.

EXPERIMENTAL

Basic carbonates of cadmium and zinc were precipitated from an aliquot of stock solutions containing cadmium-copper(II) and zinc-copper(II) present as chlorides, by adding an excess of saturated solution of sodium hydrogen carbonate sufficient to keep the copper(II) in solution. The solution was heated on a water bath and stirred occasionally for half an hour and the precipitate allowed to settle. The clear liquor was decanted through a sintered glass filter and the precipitate rinsed twice with concentrated solution of sodium hydrogen carbonate and finally transferred into the funnel and washed with hot water until free from copper(II), chlorides and alkali.

The amounts of cadmium and zinc present were further estimated by the procedure followed in the original methods [1,2]. The results are given in Tables I and II.

When copper contents were more than cadmium or zinc, they were reprecipitated to free them from copper.

Use of sodium bicarbonate as the precipitant allows estimation of cadmium and zinc without H_2S or electrolytical copper separation in copper-containing alloys.

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TABLE I

ESTIMATION OF CADMIUM IN PRESENCE OF COPPER(II)

Expt. No.	Cupric oxide taken g	Cadmium oxide taken g	Cadmium oxide found g
1	0.0318	0.0536	0.0538
2	0.0318	0.1072	0.1076
3	0.0318	0.1608	0.1612
4	0.0636	0.0536	0.0538

TABLE II

ESTIMATION OF ZINC IN PRESENCE OF COPPER(II)

Expt. No.	Cupric oxide taken g	Zinc oxide taken g	Zinc oxide found g
1	0.0318	0.0322	0.0320
2	0.0318	0.0644	0.0640
3	0.0636	0.0322	0.0324

SUMMARY

Cadmium and zinc have been separated from copper-containing mixtures of their chlorides, using sodium hydrogen carbonate as a precipitant. Cadmium and zinc are precipitated as basic carbonates while the copper(II) is retained in the solution. To the basic carbonates potassium iodide or sodium thiosulphate is added as the reagent and amounts of cadmium and zinc are estimated alkalimetrically.

RÉSUMÉ

Le cadmium et le zinc peuvent être séparés du cuivre, en solution chlorhydrique, au moyen de bicarbonate de sodium. Le cadmium et le zinc sont précipités comme carbonates basiques, tandis que le cuivre(II) reste en solution. Aux carbonates basiques, on ajoute de l'iodure de potassium ou du thiosulfate. Le cadmium et le zinc sont alors dosés par alcalimétrie.

ZUSAMMENFASSUNG

Cadmium und Zink wurden aus den Kupfer enthaltenden Mischungen ihrer Chloride mit Natriumbicarbonat als Fällungsreagenz abgeschieden. Cadmium und Zink werden als basische Carbonate ausgefällt, während das zweiwertige Kupfer in der Lösung zurückbleibt. Zu den basischen Carbonaten wird Kaliumjodid oder Natriumthiosulfat als Reagenz hinzugefügt und die Cadmium- und Zinkmenge alkalimetrisch bestimmt.

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ALIZARIN BLUE AS A SPECIFIC REAGENT FOR THE GRAVIMETRIC DETERMINATION OF COPPER

by

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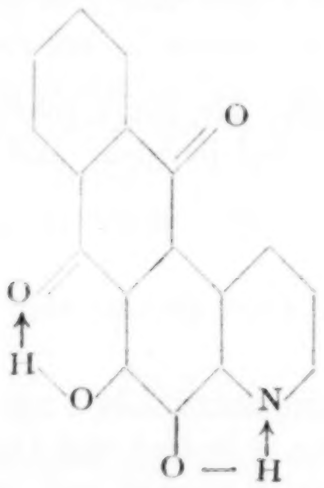
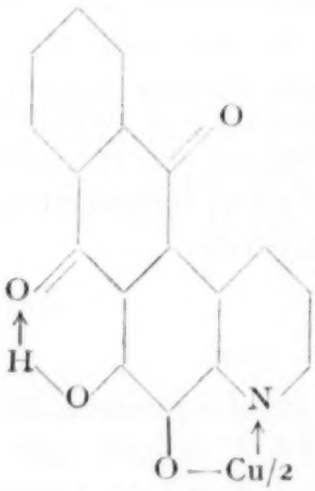
In a previous paper[1] it was pointed out that the dye alizarin blue, for which, in view of its insolubility in aqueous acids and alkali hydroxides, was assumed the chelate formula (I), reacts specifically with cupric ions. In strongly acid solutions, only this ion forms a blue crystalline precipitate when some drops of a pyridine solution of alizarin blue are added*. The copper alizarin blue formed, for which the chelate formula (II) was proposed, is extremely insoluble, as shown by its resistance against highly concentrated mineral acids as well as by its formation from highly diluted solutions. In line with this, the copper alizarin blue is not altered by sulfide ions (hydrogen sulfide or ammonia sulfide) and is also insoluble in potassium cyanide solutions which dissolve almost all water insoluble normal and complex copper salts.



(I)



(II)

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* On addition of a pyridine solution of the dye to ammoniacal solutions of $Zn^{\cdot\cdot}$, $Cd^{\cdot\cdot}$ and $Ni^{\cdot\cdot}$ salts, blue or blue green precipitates are formed, which are easily destroyed by diluted mineral acids.

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Based on the extreme insolubility of copper alizarin blue, and by means of the previous formation and extraction of copper cupferronate[2], a method for detection of traces of copper in water or metallic nickel could be elaborated. In view of the specific behaviour of alizarin blue toward copper ions and of the fact that copper alizarin blue has only a content of about 10% of copper, it seems desirable to develop a method for the gravimetric determination of copper. In the following a procedure is described which allows an exact determination of mg amounts of copper. It is highly probable that by the same way or with appropriate alterations smaller quantities of this metal may be determined microgravimetrically.

In the attempt to elaborate a gravimetric method based on the copper alizarin blue reaction, the handicap has to be overcome that the dye is only soluble to the extent of about 0.2% in pyridine. Therefore, when this solution is added to an aqueous acid copper solution, not only the blue copper salt is precipitated, but also the excess of the blue red dye. At first glance, the danger of a permanent occlusion of the dye by the precipitate could be expected. However, it was observed that, probably owing to the insolubility of the copper salt and its crystalline structure, an occlusion does not occur, anyway not to such an extent as to hinder the complete purification of the precipitate. When the precipitate containing copper alizarin blue and an excess of the dye is treated first with acetic anhydride and then with pyridine, the copper salt remains unaltered, whereas the dye is completely removed*. In this way the specific precipitation action of the dye is maintained and chemically pure precipitates are obtained.

In view of the great volume of precipitated copper alizarin blue, the amount of copper to be determined should not be greater than 2 mg. According to our experiments, the following procedure can be recommended when cupric ions are present.

Reagents

1. Saturated solution of alizarin blue in pyridine. The stable solution is obtained by dissolving an excess of alizarin blue in hot pyridine and filtering after cooling to room temperature.
2. Acetic anhydride.
3. Pyridine.

Procedure

To about 20 ml of aqueous solution containing maximally 2 mg of copper, are added 20 ml of 6 *N* sulfuric acid. The solution is heated and then the reagent solution is added dropwise. Initially the reaction is slow but, once in course, continues rapidly. When the precipitation is completed, the supernatant solution must show a reddish-blue color and remain distinctly acid. After standing 30 minutes to 1 hour, the precipitate is collected, with the aid of 3 *N* sulfuric acid, in a filter crucible of fine porous plate.

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* The solubility of the dye in acetic anhydride probably is due to an acetylation of phenolic groups. This assumption is in line with the fact that the solution in acetic anhydride does not react with copper ions, but when evaporated and treated with pyridine the reactivity is re-established.

To purify the precipitate, the following procedure is advisable: The crucible is placed in a small beaker filled to half the height of the crucible with acetic anhydride and heated (60—80°) for half an hour. It is recommendable to cover the beaker with a watch glass. Then the hot acetic anhydride is filtered through the crucible and the precipitate is washed with hot pyridine, until the filtrate shows no more blue colour. After removing the pyridine by washing with alcohol, the precipitate is dried at 100° C during 30 minutes, and weighed. The theoretical factor is 0.0991, and the results of determinations on standard samples are rather accurate as shown by a maximum error of 4% for the amount of metal present.

Determination of copper in the presence of alkali cyanide

It is well known that, due to the presence of stable complex cyanocuprous anions, practically all precipitation and colour reactions of cupric ions in solutions containing excess of alkali cyanide are masked. For the detection of copper in such solutions complete destruction of alkali cyanide is necessary. As a rule this is achieved by prolonged heating with mineral acid, a procedure not only time-consuming, but also rather disagreeable in view of the formation of volatile poisonous hydrocyanic acid. The electrolytic deposition of copper from alkali cyanide solution has the disadvantage that, together with copper, also silver, nickel, cobalt, etc., may be deposited. Furthermore, the determination of copper in amounts smaller than 2 mg is not accurate[3].

In view of the fact that only a minimal cupric ion concentration is necessary for the precipitation of copper alizarin blue, the behaviour of white cuprous cyanide, or more correctly, the cupric-cuprous system, towards alizarin blue was examined. It was stated that copper alizarin blue is immediately formed when a sulfuric acid or a pyridine solution of alizarin blue is added to a suspension of cuprous cyanide in acids. The transformation obviously is the result of the following steps:

The cuprous ions coming from the equilibrium

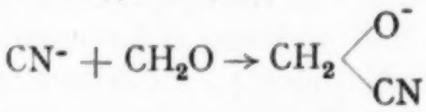
$$Cu_2(CN)_2 \rightleftarrows Cu_2^{+2} + 2\ CN^- \quad \ldots\ldots\ldots \quad (1)$$

undergo autoxidation according to

$$Cu_2^{+2} + O + 2\ H^+ \rightarrow 2\ Cu^{+2} + H_2O \quad \ldots\ldots \quad (2)$$

The cupric ions formed by (2) react immediately with alizarin blue, disturbing the equilibrium (1) which is immediately re-established. In this way, all the copper of the cuprous cyanide is transformed into insoluble copper alizarin blue. Cuprous cyanide can easily be formed from solutions containing complex cyano cuprous anions by addition of formaldehyde. Demasking occurs owing to the formation of glycolic acid nitril, according to:

$$[Cu_2(CN)_4]^{-2} \rightleftharpoons Cu_2(CN)_2 + 2\,CN^-$$



$$CN^- + CH_2O \rightarrow CH_2\begin{matrix} O^- \\ CN \end{matrix}$$

The demasking effect by means of formaldehyde has already been used[4] to obtain nickel ions from complex $[Ni(CN)_4]^{-2}$ ions.

According to our experiments, the following procedure can be recommended for the determination of copper in alkali cyanide solutions. The procedure is also valid in presence of other metal cyanide complexes.

Reagents

1. Saturated solution of alizarin blue in pyridine.
2. Formaldehyde.
3. Acetic anhydride.
4. Pyridine.

Procedure

To about 20 ml of aqueous solution containing no more than 2 mg of copper in the form of complex cyano cuprous anion, a few drops of formaldehyde are added. The solution is acidified with 20 ml of 6 *N* sulfuric acid and heated to boiling until the excess of formaldehyde is completely expelled. Then the solution of alizarin blue in pyridine is added dropwise, and the precipitate formed is treated as mentioned in the procedure above.

A set of results is shown in the Table I, in which each figure is the average of duplicate determinations.

TABLE I

DETERMINATION OF COPPER

(in presence of 200 mg of Ni^{+2} and great excess of CN^-)

Copper present mg	Copper found mg	Difference mg
2.00	2.06	0.06
1.00	1.04	0.04
0.50	0.53	0.03

References p. 343.

ACKNOWLEDGEMENT

The authors are indebted to the Conselho Nacional de Pesquisas (Brazil) for material assistance.

SUMMARY

A new method for the gravimetric determination of copper was developed, based on the specific precipitation of copper alizarin blue from highly acid solutions. The determination can be carried out in very dilute solutions up to an amount of 2 mg of Cu. Copper can also be determined in alkali cyanide solution after demasking with formaldehyde.

RÉSUMÉ

Une nouvelle méthode de dosage gravimétrique du cuivre est proposée; elle est basée sur la précipitation spécifique du composé cuivre - bleu d'alizarine, en solution fortement acide. Ce dosage peut s'effectuer en solution très diluée (jusqu'à 2 mg Cu). Le cuivre peut également être dosé, en présence de cyanure alcalin, après démasquage au moyen de formaldéhyde.

ZUSAMMENFASSUNG

Auf Grund der spezifischen Fällbarkeit von Kupfer Alizarinblau aus stark saurer Lösung wurde eine neue Methode zur gravimetrische Bestimmung von Kupfer ausgearbeitet. Die Bestimmung kann in sehr verdünnter Lösung (bis 2 mg Cu) ausgeführt werden. Die Kupferbestimmung kann auch in alkalicyanidhaltigen Losungen nach Demaskierung mit Formaldehyd vorgenommen werden.

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PARTITION PAPER CHROMATOGRAPHY OF INORGANIC CATIONS USING ALCOHOLIC KCN AS SOLVENT

by

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The many aspects of the phenomena known as chromatography have been carefully studied by a large number of workers and their conclusions have been summarised by one reviewer[1] in the following terms. The differential migration of solutes through a polyphase system is determined by the equilibria that are developed between solutes, solvent and sorbent, and this equilibria may involve solution, surface or interfacial attraction and chemical reaction including solvation and complex formation in both phases.

The following investigation was undertaken with a dual purpose, namely, to gather further information regarding the contribution of *chemical reaction* to ionic movement *and* to estimate the value of alcoholic cyanide solutions as solvents for the separation of inorganic cations.

This particular solvent was chosen in view of the fact that potassium cyanide will react with many inorganic cations in the following manner and that changes in solubility brought about by these reactions would be accentuated by the presence of the alcohol.

(1) $M^{x+} + x\,CN^- = M(CN)_x$ (Sparingly soluble)

(2) $M(CN)_x + y\,KCN$ (excess) $= K_yM(CN)_{x+y}$ (Soluble complex)

PROCEDURE

Equal volumes of standard solutions of the inorganic cations Ag^+, Pb^{+2}, Hg^{+2}, Cu^{+2}, Cd^{+2}, Bi^{+3}, Zn^{+2}, Co^{+2} and Ni^{+2} were "spotted" in similar positions on a series of rectangular paper strips prepared from Whatman No. 1 Filter Paper. These papers were suspended in an enclosed glass vessel with the lower end dipping into the alcoholic solvent which contained concentrations of KCN varying from $4N$ to $10^{-4}N$. After a standard period of development the papers were removed and the new position of the cations located by exposure

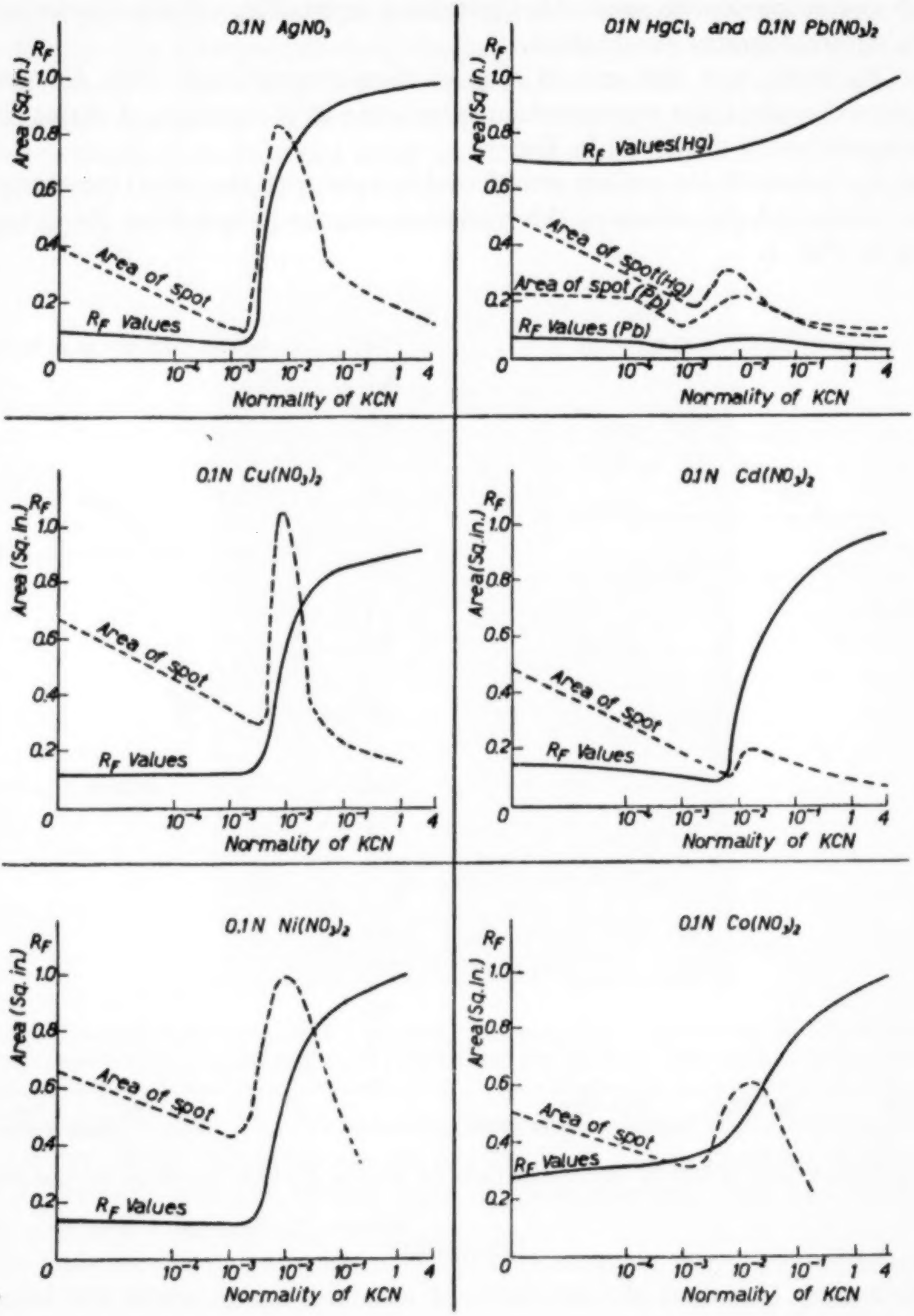

Fig. 1. The effect of varying concentrations of KCN in the solvent on the R_F value and area of spot produced on paper chromatograms of inorganic cations.

to H_2S or treatment with some other suitable reagent. Fig. 3 illustrates the nature of the chromatograms so obtained.

The R_F value and the area of each of these "spots" were then determined and plotted against the concentration of cyanide in the solvent. A series of the resulting curves is displayed in Fig. 1.

The R_F values of the cations were found to vary with the initial concentration of the solute and the extent of this variation may be judged from the examples shown in Fig. 2.

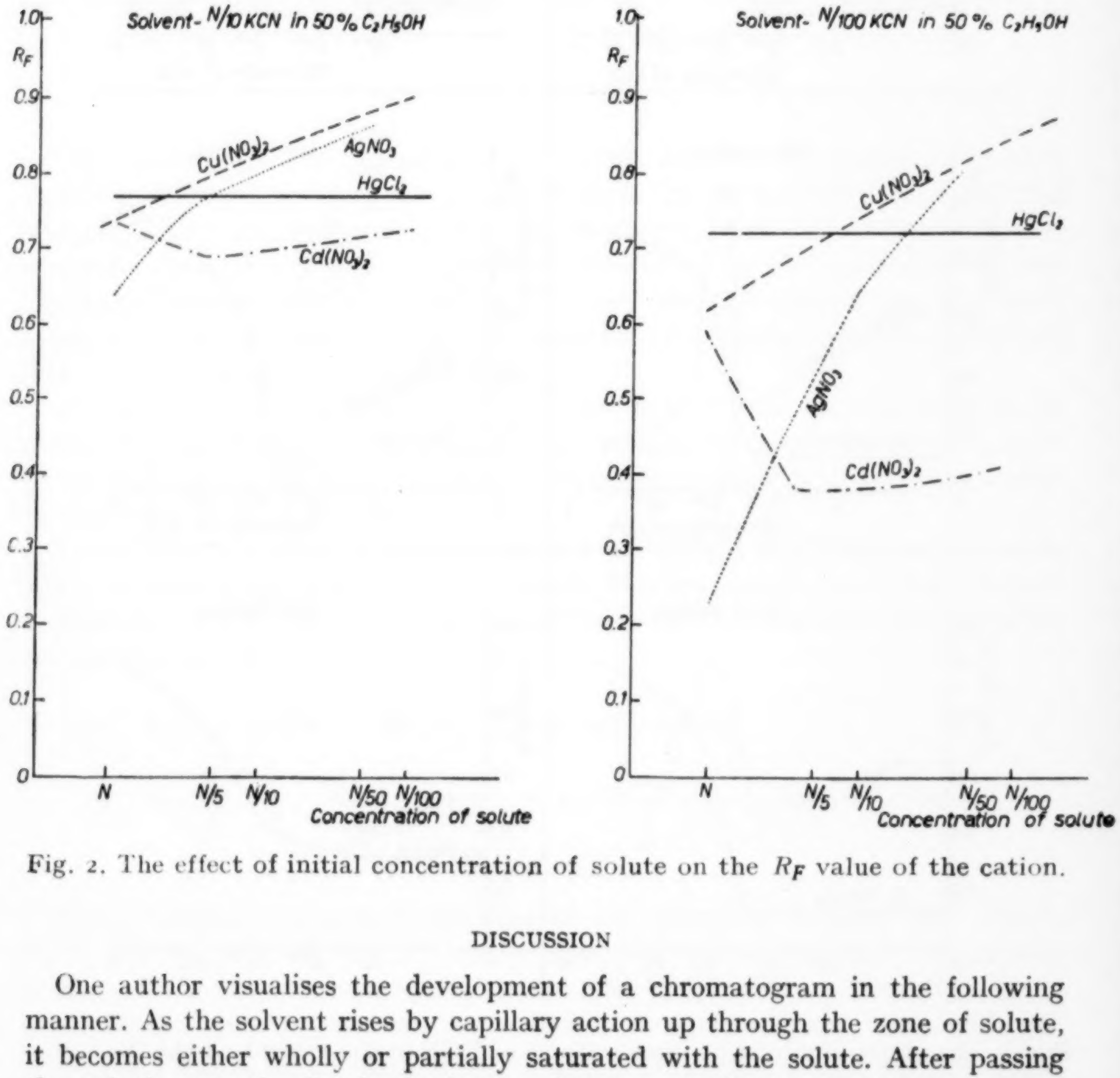

Fig. 2. The effect of initial concentration of solute on the R_F value of the cation.

DISCUSSION

One author visualises the development of a chromatogram in the following manner. As the solvent rises by capillary action up through the zone of solute, it becomes either wholly or partially saturated with the solute. After passing through the zone the dissolved solute tends to pass again out of solution at a rate dependent on the relative partitional distribution which exists between the solvent and the non-mobile phase. The greater the solubility of the ion in the solvent, the further it is transported along the paper by a given volume of that solvent[2].

The use of a chemically active solvent adds another variable factor to the equilibrium conditions. When the solute is taken into solution by the flow of solvent, chemical reaction can occur and the reaction products may differ widely in solubility. The nature and extent of the interaction will be controlled to a large degree by the proportions of solute and reactive ions present.

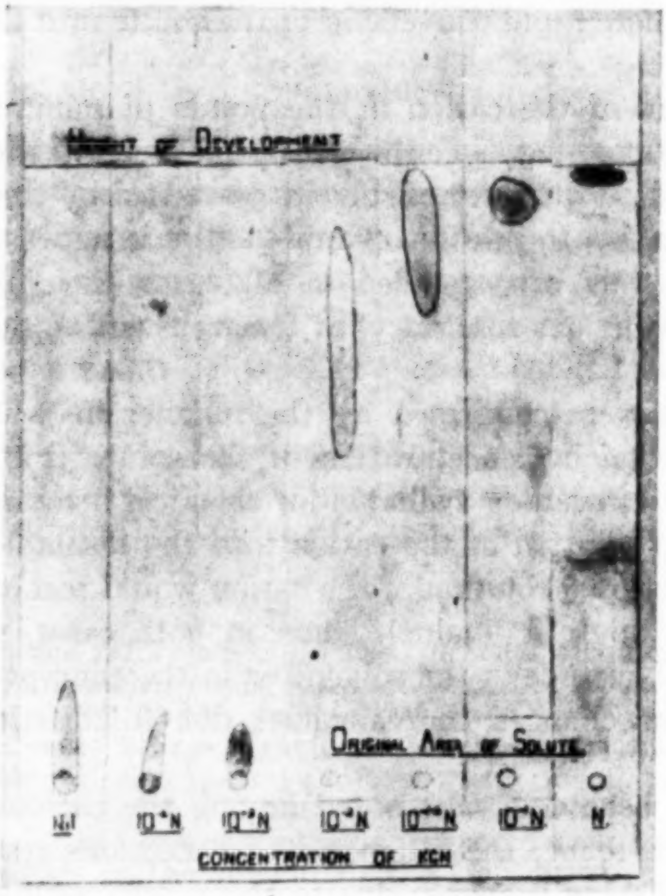

Fig. 3. Chromatograms of 0.1*N* $AgNO_3$ showing the variation in R_F value and area of spot with increasing concentrations of KCN in the 50% ethanol solvent.

The results obtained in this investigation can be quite satisfactorily explained by this hypothesis. When the solvent was aqueous alcohol, solubility of the solute was appreciable and the cations were diffused upwards. This yielded a large spot area and a marked R_F value.

The addition of small amounts of KCN to the solvent was sufficient to convert some of the solute to the insoluble cyanide which immediately passed out of solution leaving fewer ions to diffuse upwards. This in turn resulted in a smaller diffused spot and a lower R_F value.

At the critical point where just sufficient cyanide was present to completely convert the solute to the sparsely soluble cyanide, migration of ions was slight and the R_F value and area of spot for the cation showed a definite minimum.

The passage of slightly stronger solvents caused some of the sparsely soluble cyanide to be returned to solution as the complex. This partial formation of the complex resulted in higher R_F values but also led to larger spot areas. The extensive diffusion of the ions reached a maximum when there was just sufficient cyanide present to completely convert the solute into the soluble complex.

More active solvents resulted in higher R_F values (the solubility of the complex being increased inter alia by the common ion effect) and the spot area gradually decreased with the more rapid conversion of the solute into the soluble complex. (*cf.* Fig. 3).

The chemical form of the cation at the points of minimum and maximum inflexion in the area curves was confirmed by mathematical computation. After the flow of the standard quantity of solvent (governed by the height of development) the ratio of cation to possible cyanide ion present was calculated. Within experimental limits this corresponded in all cases (except cadmium) to the stoichiometrical proportions necessary to form either the cyanide or the most stable complex salt.

These conclusions were confirmed by the manner in which the R_F values changed with variation in concentration of the solute (Fig. 2). With a given solvent, the amount of cyanide available for chemical reaction may be sufficient to convert a normal solution of the cation into the insoluble cyanide (low R_F value) whilst a decinormal solution of the cation would react to form the soluble complex compound (high R_F value). Thus in both cases, variations in either the concentration of cyanide in the solvent or in the concentration of the solute resulted in profound changes in R_F values due to differing products of the chemical action.

Some anomalous behaviour was noted among the cations examined. In the cases of lead and mercury, the alteration of conditions resulted in but minor variations in R_F. This is probably due to the sparse solubility of lead salts in alcohol and the very small degree of ionisation of mercuric salts in solution. Bismuth, which does not react with potassium cyanide, remained unmoved on the chromatograms. Cobalt was unique in that its cyanide compound $Co(CN)_2$ was more soluble in the solvent than the nitrate.

The strange behaviour of cadmium could arise from its ability to form auto complexes of the nature $Cd[Cd(CN)_4]$ as well as the salts $Cd(CN)_2$ and $Cd(CN)_2 \cdot 2KCN$. A number of ionic forms could therefore contribute to the equilibria.

Since the amount of cyanide brought into contact with the solute will be proportional to the volume of solvent which flows through the initial zone, variation in the height of development can produce marked changes in the composition of the reaction products with the subsequent variation in solubilities and R_F values.

As a cation separating medium, alcoholic cyanide solutions were quite unsuitable. The solvents which gave the largest variations in R_F between the cations also gave the most diffuse spots and when separating a mixture these spots merged together. The changes in R_F affected by varying the concentration of solute would also make identification of the mixture components quite difficult even if an initial separation could be accomplished.

It appears that chemical reaction between the solvent and solute can have a profound effect on ionic movement and the magnitude of this effect made alcoholic KCN solutions completely unsatisfactory as a solvent for the separation of inorganic cations by paper chromatography.

CONCLUSIONS

Alcoholic KCN solutions did not prove to be satisfactory solvents for inorganic cations but their use did emphasise the role that may be played by chemical reaction in partition chromotography. Where such chemical reaction is likely to be a major factor contributing to the differential migration of the ions (as in this investigation), it is reasonable to expect the R_F values of the ion to vary with any changes in the ratio of solute to active solvent concentrations.

ACKNOWLEDGEMENT

The author wishes to acknowledge with thanks the advice and assistance rendered by W. R. WALKER during the course of this investigation.

SUMMARY

In order to gain some information on the role that chemical reaction may play in differential ionic movement, paper chromatograms of the inorganic cations Ag^+, Pb^{+2}, Hg^{+2}, Cu^{+2}, Cd^{+2}, Bi^{+3}, Zn^{+2}, Co^{+2} and Ni^{+2}, were developed using alcoholic KCN as solvent. This solvent was chosen since it was capable of reacting with the cations to form both a sparsely soluble metal cyanide and a soluble cyanide complex.

An examination of these chromatograms indicated that variation of either the concentration of cyanide in the solvent or the concentration of the cation in the solute, resulted in widely differing R_F values. The area of the developed spot also varied with different ratios of these two variables. It was then calculated that the R_F value and the area of spot were functions of the relative amounts of metallic cyanide and cyanide complex formed by chemical reaction.

RÉSUMÉ

En vue d'étudier le rôle des réactions chimiques sur les différents mouvements ioniques, l'auteur examine les chromatogrammes de cations inorganiques: Ag^+, Pb^{+2}, Hg^{+2}, Cu^{+2}, Cd^{+2}, Bi^{+3}, Zn^{+2}, Co^{+2} et Ni^{+2} développés avec une solution alcoolique de cyanure de potassium comme solvant. Le choix du solvant est basé sur le fait qu'il peut réagir avec les cations pour former un cyanure métallique partiellement soluble et un complexe cyané soluble. Ces chromatogrammes montrent des variations considérables de R_F pour des différences de concentration de cyanure dans le solvant ou du cation dans le soluté. La surface des taches développées varie aussi avec ces concentrations. Il est ensuite démontré que la valeur de R_F et la surface de la tache sont fonctions des teneurs relatives en cyanure métallique et en complexe cyané formés.

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ZUSAMMENFASSUNG

Um einige Kenntnis zu gewinnen über die Rolle, die eine chemische Reaktion bei der differentiellen Ionenbewegung spielen kann, wurden die Papierchromatogramme der anorganischen Kationen Ag^+, Pb^{+2}, Hg^{+2}, Cu^{+2}, Cd^{+2}, Bi^{+3}, Zn^{+2}, Co^{+2} und Ni^{+2} unter Benutzung von alkoholischem KCN als Lösungsmittel entwickelt. Dieses Lösungsmittel wurde deshalb gewählt, da es fähig ist mit den Kationen sowohl unter Bildung eines wenig löslichen Metallcyanids als auch eines löslichen Cyanidkomplexes zu reagieren.

Eine Prüfung dieser Chromatogramme zeigte, dass eine Änderung sowohl der Cyanidkonzentration im Lösungsmittel als auch der Kationenkonzentration in dem zu lösenden Stoff sehr verschiedene R_F-Werte ergab. Die Fläche der entwickelten Tüpfel variierte ebenso mit dem verschiedenen Verhältnis dieser zwei Variablen. Es wurde dann errechnet, dass die R_F-Werte und die Fläche der Tüpfel Funktionen der relativen Mengen der durch die chemische Reaktion gebildeten Metallcyanide und Cyanidkomplexe waren.

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THE DETERMINATION OF MICROGRAM QUANTITIES OF FLUORIDE

I. THE USE OF THE ALUMINIUM-HAEMATOXYLIN COMPLEX

by

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1. INTRODUCTION

Much effort has been expended in recent years in attempts to derive satisfactory methods for determining fluoride on the microgram scale. The thorium nitrate titration which has since its introduction by Willard and Winter[1] been the standard method gives rise to many difficulties at low concentrations of fluoride and a number of attempts to improve it have been made[2, 3, 4]. Generally the method can be made to work provided exact experimental conditions are laid down and the tests are carried out by an experienced analyst but even so it is unreliable at low concentrations of fluoride. Other methods make use of the suppression by fluoride of certain colour reactions, the most notable in current use being the reaction of fluoride with the iron complex of 5-sulpho-salicylic acid,[5, 6, 7] with iron thiocyanate[8 à 13] or with zirconium alizarin sulphonate[14], but these are not satisfactory at really low concentrations of fluoride ion. A very complete review of methods for fluorine and fluoride analysis up to 1950 is given in a recent publication by McKenna[15].

In seeking a more satisfactory method for the determination of amounts of fluoride (1-10 μg/ml) we examined the effect of this ion on a number of colour reactions. Only the reaction between aluminium and ammonium tricarboxylate (aluminon) gave any promise of providing the basis of a successful method. This reaction was found to be quantitatively affected by fluoride ions but the effect was small and since the fading of the aluminium complex itself was sufficiently rapid to cause trouble it was considered that the experimental error of such a method would be relatively high. It was clear however that fluoride at low concentrations could successfully complex aluminium and prevent its reacting with the reagent, and it was thus probable that if a sufficiently sensitive reagent for ionic aluminium could be found, then a satisfactory method for fluoride could be developed. Such a reagent was found in haematoxylin which reacts only with ionic aluminium to give a purple coloured complex which has itself been

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used in estimating this element[16]; this complex proved very sensitive to fluoride, and forms a good basis for determination of the element (ion). The aluminium-haematoxylin complex has not proved very successful as a means of determining aluminium since the complex formed from standard amounts of reagent and aluminium does not give a reproducible colour density. However for fluoride determination this does not matter since a single solution of complex is used, one aliquot being treated with fluoride and subsequently matched against another aliquot of untreated complex; in this manner variations due to the behaviour of a solution of complex are eliminated. (A method for determining fluoride down to a concentration of 0.02 μg per ml has been developed). During the development of the method described here we discovered that a similar method had been used by OKUNO[17] for the determination of fluoride in water.

2. EXPERIMENTAL

Several considerations of practical and theoretical importance are involved. These will each be presented in turn with supporting experimental data. The method adopted will then be described.

2.1. *Formation and properties of the aluminium-haematoxylin complex*

In alkaline solution (optimum pH 8.0-9.0) aluminium reacts with haematoxylin to give a purple coloured complex. The reaction also takes place at pH values down to about 4.2 but becomes very slow when conditions become acid. This complex is relatively stable down to a pH of about 4.2, below this it becomes increasingly unstable; it shows a similar lack of stability at a pH greater than 9.0. The instability is due to different causes at the different pH values and these phenomena will be discussed fully in a subsequent paper. In the pH range 4.2-8.0 the complex is liable to precipitate on standing but this can be eliminated by the addition of a stabiliser such as gum arabic, starch etc. If therefore aluminium and haematoxylin are mixed in the presence of gum arabic at pH 8-9 and acid is then added to adjust the pH to a suitable value, the absorption at 5700 A (Ilford filter 605) gives a measure of the amount of complex formed and hence of the amount of aluminium in the solution. This is the basis of a method of determining aluminium which has been used by several authors[16, 18-21] although the reproducibility is not considered satisfactory.

When aluminium and haematoxylin are mixed at pH 8-9 and the absorbancy of the solution (Ilford filter 605) is plotted against time (Fig. 1), the absorbancy reaches a peak after fifteen to twenty minutes. This peak is not always of constant height; the height appears to depend not only on both the concentrations of aluminium and haematoxylin and their relative proportions, but on other factors also particularly pH (*cf.* section 2.3), which is probably the reason why GINSBURG[22] found this method unsuitable for quantitative determination of aluminium.

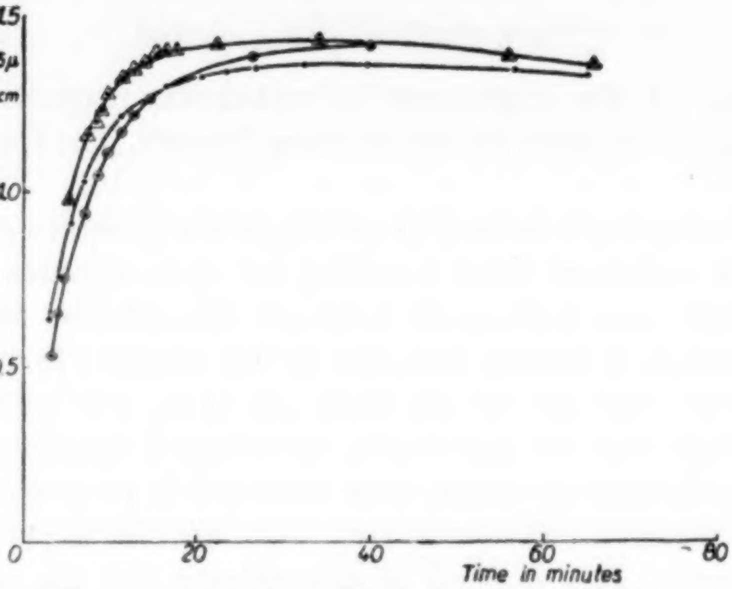

Fig. 1. Rate of formation of complex. Plots for three different experiments are shown.

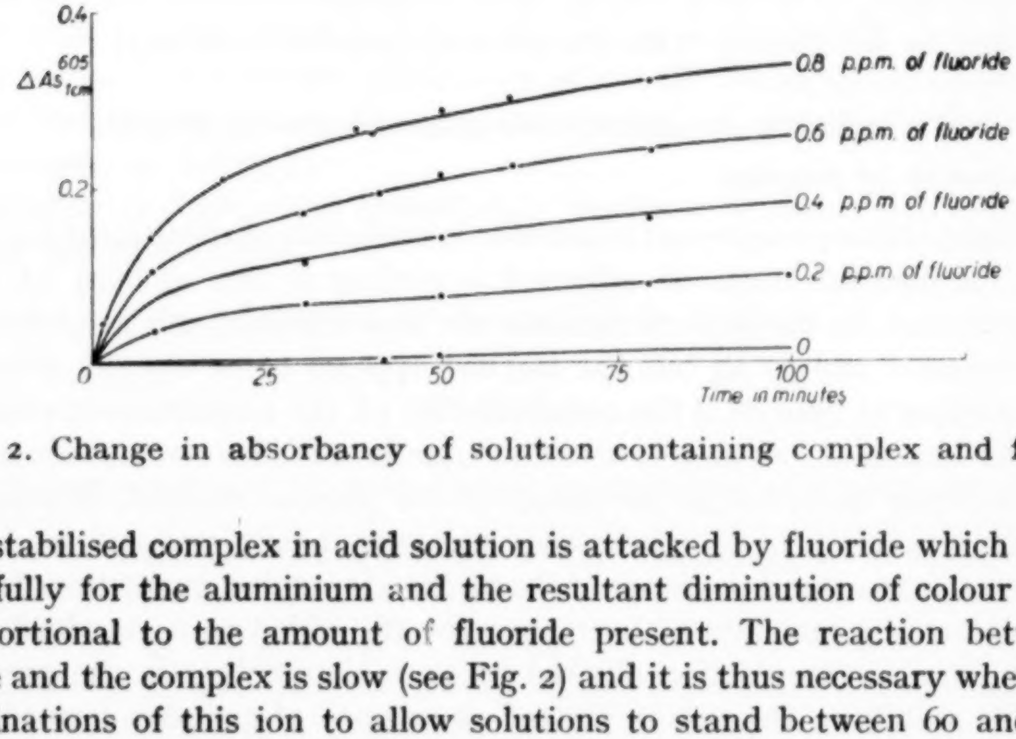

Fig. 2. Change in absorbancy of solution containing complex and fluoride.

The stabilised complex in acid solution is attacked by fluoride which competes successfully for the aluminium and the resultant diminution of colour intensity is proportional to the amount of fluoride present. The reaction between the fluoride and the complex is slow (see Fig. 2) and it is thus necessary when making determinations of this ion to allow solutions to stand between 60 and 75 min before taking a reading of the change of absorbancy. This seems to be due mainly to the time taken for the aluminium fluoride complexes to attain equilibrium as BROSSET AND ORRING[23] under similar conditions found that about one hour was required for the system to reach equilibrium. It will be noted (Fig. 2) that even when the reaction between the complex and the fluoride ion appears complete a slow but steady fading still appears to be taking place; this is due to slow decomposition of the complex and the reason for it will be discussed in a forthcoming paper.

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2.2. *Outline of the method*

The properties of the aluminium-haematoxylin reagent already described are the basis of a new method for determining fluoride. The following is an outline of the method.

A solution of complex is formed at pH 8-9 in the presence of a small amount of gum arabic as stabiliser. After standing for 15-20 minutes the pH is adjusted to a suitable value (4.9) with acetic acid and the solution allowed to stand for a further 15 minutes. A known quantity of this complex is added to the sample containing fluoride buffered to the same pH (4.9). The mixture is allowed to stand for one hour and the absorbancy determined against a blank containing no fluoride. The decrease in colour thus measured is proportional to the fluoride present in the sample. At the same time a calibration is prepared using known amounts of fluoride. This method of determining not the absorbancy but the change in absorbancy using a fluoride-free solution of complex as a standard eliminates any errors which may arise due to the variation in absorbancy of prepared solutions of complex. In addition the instrument may be zeroed on the solution containing no fluoride and the small difference between the two solutions can therefore be determined with the greatest possible accuracy.

2.3. *Conditions for quantitative determination of fluoride*

a. *Concentration of complex*

The amount of complex present in solution is obviously of the utmost importance and its concentration must be adjusted according to the amount of fluoride to be determined. In the present instance we have confined our attention to the region between 0 and 50 μg but the method appears to be equally suitable for larger quantities of fluoride if the concentration of the aluminium-haematoxylin complex is increased, although we would prefer to dilute more concentrated samples to bring them within the range of the present method. Working with a more dilute solution of complex raises unexpected problems and we have not as yet been able to extend the range of the method to smaller quantities of fluoride.

When increasing amounts of haematoxylin are added to a standard amount of aluminium and the reaction allowed to go to completion in the presence of gum arabic stabiliser, the results plotted as amount of complex formed against haematoxylin added (*cf.* Fig. 3) indicate that the ratio of haematoxylin to aluminium is 1.33. Since it is obvious that any excess aluminium will decrease the sensitivity of the reagent for fluoride, at least enough haematoxylin must be present to combine with all the aluminium and normally an excess of this substance is added. In practice it is found advisable to keep the excess of haematoxylin to a minimum, the actual ratio of haematoxylin to aluminium used is 1.37. This question will be further dealt with in Part III of the present series of papers.

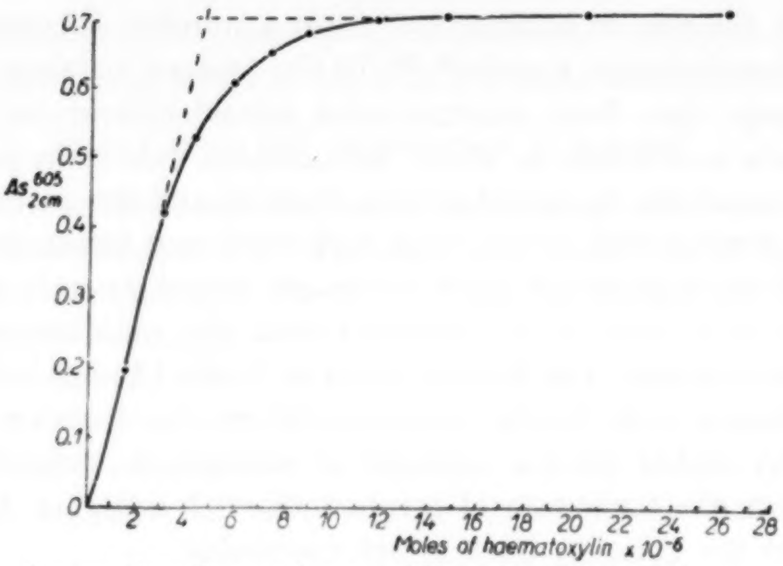

Fig. 3. Amount of complex formed on adding haematoxylin to $3.7 \cdot 10^{-6}$ moles of aluminium.

b. *The effect of pH variation*

As has already been mentioned the aluminium-haematoxylin complex is relatively stable in acid solution above a pH of 4.2 the stability increasing as the pH. The effect of fluoride on the complex is found to decrease with increasing pH as is shown in Table I.

The amount of aluminium immediately available to react with fluoride will depend on the equilibrium.

$$\text{Complex} \rightleftarrows \text{Haematoxylin} + \text{Al}. \qquad (1)$$

TABLE I

THE EFFECT OF PH ON THE DECREASE OF COLOUR INTENSITY (ABSORBANCY) OF THE ALUMINIUM-HAEMATOXYLIN COMPLEX PRODUCED BY KNOWN QUANTITIES OF FLUORIDE

pH of solution	Decrease in absorbancy × 10^3 µg of F added per 25 ml of solution					Absorbancy × 10^3 of fluoride free solution against water	
	5	10	15	20	25		
4.6	147	293	425	519	597	805	
4.8	117	252	379	490	593	1036	Figures in this column give a measure both of the amount of complex and its stability.
4.92	113	257	374	496	588	1158	
5.2	119	185	282	360	445	>1300	

The absorbancy was measured on a Hilger Spekker absorptiometer using Ilford 605 filters and 2 cm cells. The complex was made up in the same way and with the same quantities of material in each case (*cf.* section 2.5).

Aluminium and fluoride in solution will form a number of compounds AlF_n^{+3-n} where n has values between 1 and 6[23, 24]. In the present instance those possessing a negative charge can, from concentration considerations be neglected. Now the more acid the conditions in which the complex exists the more readily aluminium will be available to combine with fluoride and the more likely it is that the compounds formed will have a high Al/F ratio and hence the more sensitive the method will be. Conditions must be chosen therefore such that the solution of the complex is as acid as is consistent with the maintenance of a suitable concentration of complex. The figures given in Table I indicated 4.9 as probably the most satisfactory pH. Under these conditions the fluoride formed appears to be AlF_2^+. At higher pH the amount of aluminium immediately available appears to favour the formation of compounds with a higher Al/F ratio, whilst at a lower value the complex itself is not too stable.

c. *The effect of temperature*

All the reactions involved will be speeded up with increase of temperature but in general accurate temperature control is not necessary and the operations can be satisfactorily carried out at room temperature. Normally fluoride is separated from interfering ions by the distillation technique of WILLARD AND WINTER[1]; in this case it is essential to ensure that the samples of distillate and the calibration solutions are all brought to the same temperature prior to addition of the aluminium-haematoxylin complex, and that there is no marked difference in temperature between any of the solutions during the hour which they must stand prior to the measurement of the amount of complex destroyed by fluoride.

Where results are required quickly the period of standing may be shortened by bringing the solutions to a suitable higher temperature and maintaining them at this temperature until ready for measurement. (Fig. 4 shows the effect of raising the temperature on the ratio of reaction between fluoride and complex.)

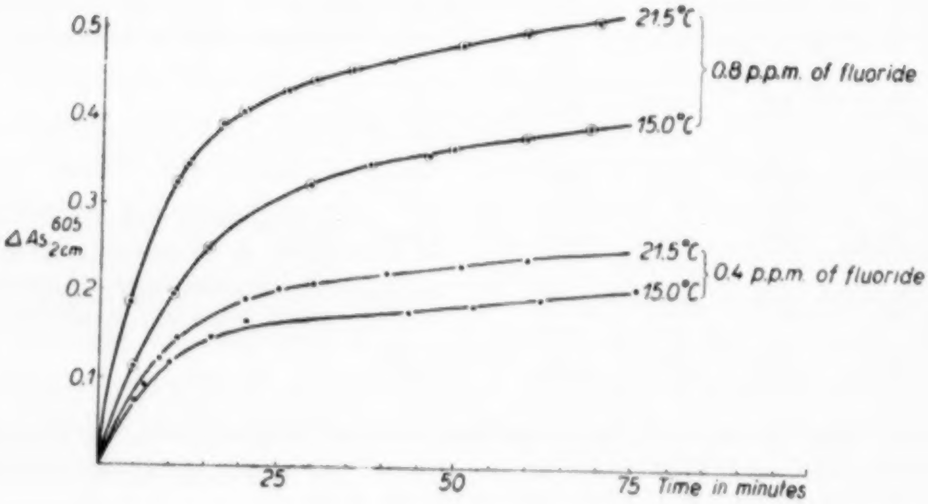

Fig. 4. Dependence on temperature of the rate of fading.

In using this technique some loss of accuracy may be found due to unequal cooling during actual measurement, but this is usually unimportant.

2.4. *Choice and preparation of reagents*

It is most important that reagents should be free as far as possible from fluoride, aluminium, and other interfering substances. Difficulties arise if certain of the reagents used are not prepared in the correct manner. These difficulties and means of overcoming them are described below.

Haematoxylin is described in American literature as a white crystalline solid but most products available in England do not attain a similar standard of purity. The best product available is Hopkins and Williams 'Revector' preparation for use as indicator or microscopical stain, but even this is somewhat discoloured.

Early experiments in preparing a solution of this substance showed that the normal procedure of dissolving in warm water did not give solutions of a strength which could be reasonably repeated and it was found more satisfactory to dissolve the material in a minimum of alcohol and dilute to the required volume with cold water.

The literature suggests that a solution of haematoxylin keeps satisfactorily for about a week only. Our observations indicated that this was probably due to slow oxidation. The oxidation of haematoxylin to haematein involves the loss of two atoms of hydrogen and it was thought that if as is possible the reaction mechanism involves a primary ionisation step, then haematoxylin would prove to be more stable in acid solution. This deduction proved correct and acid or acid buffered haematoxylin keeps quite satisfactorily for up to six weeks. These findings are confirmed by HOUGHTON[20].

Solutions of haematoxylin are susceptible to mild attacks of mould growth but this can easily be prevented by additions of small quantities of (0.05%) of chloroform about once a week or better by adding a crystal of thymol when making up the solution.

Ammonium carbonate

During our experiments certain anomalous results were obtained when changing from one supply of this reagent to another. Investigation showed that this was due to pH variation resulting from changes in the ammonia content of solutions prepared from this material.

It appeared that with the material available it was not possible to prepare solutions as strong as those used by HATFIELD[16] and that different methods of preparation of a saturated solution resulted in considerable variation in ammonia content. It was found that better results could be obtained by using a solution of ammonium carbonate which was not quite saturated but the strength of which could be readily reproduced.

Whilst the pH (8-9) at which the aluminium-haematoxylin complex is formed was obtained with any ammonium carbonate solution of strength between 10% and saturation, the pH obtained on adding to a nearly saturated ammonium carbonate a standard amount of acetic acid varied considerably (4.6-5.2) for quite small changes in ammonia content, a point of the utmost importance since the ammonia content of these solutions falls steadily with time, and accurate control of pH is essential in the method (*cf.* section 2.3b), for this reason pH values should always be checked with a meter.

Gum arabic

Samples of gum arabic vary considerably and it is difficult to make a solution with accurately reproducible properties. It is important to add sufficient of this material otherwise the stabilising action on the complex is not complete; 3 ml of 5% solution in water is usually satisfactory. The efficiency of a solution deteriorates on keeping and a preparation should not be used if it is more than a week old.

It has been found advisable with new batches of gum arabic to check the amount required to stabilise the acid aluminium-haematoxylin complex. A 5% solution is prepared and a solution of complex made up using 3 ml of the gum arabic; if the gum arabic has correct properties the change in absorbancy of the solution of complex over a period of two hours should be negligible. Should the absorbancy decrease the addition of a greater quantity of gum arabic may achieve the desired stability but it is considered that such a material is unsatisfactory and a fresh batch should be used.

Acetic acid

All acetic acid tested appears to be of a standard quality and no effect due to variation in purity or composition has been noted.

Distillation acid

For separation of fluoride by distillation as hydrofluosilicic acid, sulphuric, perchloric, or phosphoric acids can be used. They can be freed from fluoride if necessary by passing steam through them at 145-150° C.

Perchloric and phosphoric acids interfere with the method to some degree if they are present in the distillate to the extent of more than a few mg. For this reason sulphuric acid which does not interfere with the method is preferred whenever possible.

2.5. *Method*

A. *Special reagents*

(i) Standard fluoride solution.

Dissolve 0.5525 g of sodium fluoride in water and dilute to 250 ml.

Dilute 1 ml of this solution to 100 ml.

1 ml = 10 μg F.

The purest available material should be used; that supplied by BAKER AND ADAMSON to A.C.S. specification is suitable.

(ii) Standard aluminium solution.

Dissolve 1.867 g 'AnalaR' quality aluminium sulphate in water and dilute to 100 ml.

1 ml = 1.11 mg Al.

For use dilute 10 ml of the above solution to 100 ml.

1 ml = 111 μg Al.

(iii) 5% Gum arabic in water.

Dissolve 5 g of finely crushed solid in approximately 80 ml of freshly boiled water at 70° C (ca). Filter while still hot through glass wool and dilute to 100 ml with freshly boiled water. It is recommended that solutions more than a week old should not be used.

(iv) Ammonium carbonate solution.

Dissolve 20 g of a fresh sample of 'AnalaR' quality ammonium carbonate in 100 ml of water. The solid should be placed with water in a stoppered bottle. No heating should be used to dissolve it.

(v) Ammonium acetate buffer solution.

Dilute 25 ml 'AnalaR' quality glacial acetic acid to about 275 ml with water add 15 ml of 18M ammonia mix thoroughly and cool to room temperature. Adjust the pH to 4.9, using a meter, by adding either ammonia or acetic acid. Dilute to 300 ml.

(vi) Haematoxylin solution 0.1%.

Dissolve 0.25 g of a suitable preparation (see section 4.a) in 2.5 ml of industrial methylated spirit and add the solution to a mixture of 200 ml of water, 2 ml of ammonium acetate buffer and one crystal of thymol. Dilute to 250 ml with water.

B. *Procedure*

(i) Separate the fluoride from interfering ions by distillation from sulphuric, perchloric or phosphoric acid in the presence of silica according to the method of WILLARD AND WINTER[1]. Collect about 160 ml of distillate.

(ii) Neutralise the distillate to phenolphthalein with 0.1M sodium hydroxide. Record the volume of the neutralised solution and the volume of alkali used.

(iii) Prepare a blank solution by neutralising a volume of 0.1M sodium hydroxide, equal to that used in step (ii) with 0.05M sulphuric acid using phenolphthalein as indicator. Dilute the solution with water to a volume equal to that of the neutralised distillate.

(iv) Place 25 ml of the neutralised distillate in a 50 ml volumetric flask, and 25 ml of blank solution in a second 50 ml flask. Add 2 ml of acetate buffer to each flask and mix the contents thoroughly.

(v) Into each of the flasks pipette 20 ml of freshly prepared aluminium-hae-

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matoxylin reagent, make up to the mark with water and mix the contents thoroughly. Allow the solutions to stand for one hour.

(vi) Measure the difference in absorbancy between the two solutions using radiation of 5700 A.

The Hilger Spekker Absorptiometer with Ilford 605 filters and a 2 cm cell may conveniently be used.

(vii) Determine the number of μg of fluoride in the sample solution by reference to a calibration curve.

C. *Preparation of aluminium-haematoxylin reagent*

To 250 ml of water add in order the following, mixing well after each addition:

(i) 3 ml of 5% gum arabic (*cf.* section 2.4).
(ii) 5 ml of standard aluminium solution.
(iii) 5 ml 20% ammonium carbonate.
(iv) 10 ml of 0.1% haematoxylin.

Allow the solutions to stand for 15 minutes then add with thorough stirring 6*M* acetic acid until the pH is 4.9 (using a pH meter) and allow the solution to stand a further 15 minutes before using.

It is most important to stir thoroughly whilst adding the acetic acid since local concentration of acid destroys the complex and because as much as possible of the released carbon dioxide should be removed.

D. *Calibration*

(i) Into each of five stoppered measuring flasks (numbered 1-5) pipette 2 ml of ammonium acetate buffer solution.

(ii) Add standard fluoride solution to the flasks to give fluoride content as follows:

Flask No.	1	2	3	4	5
μg, F^-	0	5	10	20	25

(iii) Make volume of each flask up to about 25 ml with water and mix the contents thoroughly.

(iv) Pipette 20 ml of aluminium-haematoxylin reagent into each flask, make up to 50 ml with water and mix the contents thoroughly. The whole of this last operation must be carried out as quickly as possible. Allow the solution to stand for one hour.

(v) Measure the difference in absorbancy between each of the fluoride containing flasks and that containing none using radiation of wave length 5700 A.

The Hilger Spekker Absorptiometer with Ilford 605 filters and a 2 cm cell may conveniently be used as follows: — With the fluoride-free solution in the cell and the drum set to 0.100, adjust the instrument to give zero galvanometer deflexion.

Place the other solutions, in turn, in the same cell, and adjust the drum for zero galvanometer deflexion.

(vi) Plot absorbancy against fluoride content to give a calibration graph which should be a straight line.

2.6. *Recoveries using the method*

Separation of fluoride from water solutions containing known amounts of fluoride, added as sodium fluoride and determination using the new reagent gave results which are shown in Table II.

TABLE II

Fluoride added in μg	Fluoride recovered in μg									Mean Recovery
25	23	25	24	27	25	27	24	24		99.5 ± 8%
50	51	50	51	51	50	48.5	48	51	51	100 ± 5%
75	74	74	78	77	72					100 ± 4%
100	96	95	94.5	97						95.5 ± 2%

These results were considered satisfactory but it was thought that the new method should be checked against the well tried thorium nitrate titration method. This gave rise to certain difficulties in that the presence of sulphuric acid in the distillate interfered with the latter method and perchloric acid with the aluminium-haematoxylin reagent. However by taking great care with the control of distillation temperature and rate of distillation it was found possible to produce distillates so nearly free of perchlorate ions that no effect on the aluminium-haematoxylin reagent could be observed. Accordingly distillates prepared in this manner were divided and the fluoride content determined by both methods. Results are shown in Table III.

TABLE III

COMPARISON OF FLUORIDE RECOVERIES BY ALUMINIUM-HAEMATOXYLIN AND THORIUM NITRATE TITRATION METHODS. DISTILLATES OBTAINED FROM PERCHLORIC ACID

Fluoride added in μg	Fluoride recovered by aluminium-haematoxylin method, in μg	Fluoride recovered by thorium nitrate titration in μg
25	16*	17*
25	17*	15*
25	25	25
50	48	51
75	72	75
100	84*	85*
100	96	94

References p. 368.

The figures marked with an asterisk are low due to too low distillation temperature resulting from the attempt to keep the perchloric acid in the distillates to a minimum. The lost fluoride was subsequently found in the distillation flask.

The method was finally applied to a number of readily available chemicals and results obtained are shown in Table IV.

TABLE IV

EXAMPLES OF RECOVERY OF FLUORIDE ADDED TO VARIOUS MATERIALS

Materials	Amount grams	Fluoride added µg	Fluoride found µg	Mean Recovery %
Chrome alum	10	0	19	
		0	19	
		50	65	
		50	71	97
		100	118	
		100	113	
Copper sulphate $CuSO_4.5H_2O$	10	0	0	
		0	2	
		50	55	
		50	52	101
		100	105	
		100	98	
Nickel sulphate $NiSO_4.6\text{-}7H_2O$	10	0	7	
		0	1	
		50	53	97
		50	50	
		100	98	
		100	98	
Magnesium sulphate	10	0	21	
		0	23	
		0	16	
		50	73	
		50	68	
		50	74	100
		100	115	
		100	119	
		100	121	
Sodium hydroxide	25	0	13	
		0	7	
		0	3	
		50	53	
		50	52	92
		50	53	
		100	111	
		100	95	
		100	101	

References p. 368.

2.7. *Precision of method*

Two similar experiments were used to determine the precision of the method.

Exp. I. The reproducibility of the method was determined on blank solutions at fluoride levels of 0, 1 and 2 μg and the standard deviation determined. Six determinations were carried out at each level.

Exp. II. A calibration was carried out on a blank solution between 0 and 30 μg of fluoride.

The results were plotted, the best straight line was drawn through the points, and the deviation of the points from the line measured as the error. From these figures the standard deviation was calculated. Two such calibrations were carried out.

The results obtained are shown in Tables V and VI.

TABLE V

DETERMINATION OF PRECISION. EXP. A

Fluoride content μg	Standard Deviation μg
Nil	0.25
1	0.50
1	0.25
2	0.50

TABLE VI

DETERMINATION OF PRECISION. EXP. B

	1st calibration		2nd calibration	
Fluoride μg	Absorbancy $\times 10^3$	Error $\times 10^3$	Absorbancy $\times 10^3$	Error $\times 10^3$
0	0.00	+8		—2
1	7	+1	10	nil
2	16	—4	22	nil
3	32	—3	33	—3
4	53	+3	46	—3
5	62	—3	59	—3
10	131	—6	125	—1
15	217	+6	199	+8
20	283	—1	256	+2
30	432	+1	380	—1
Standard deviation = 0.27 μg			Standard deviation = 0.25 μg	

References p. 368.

2.8. *Interferences*

Although fluoride is normally freed from the majority of other ions by distillation it was thought probable that in certain cases the aluminium-haematoxylin method might be used directly, the ions causing interference were sought. The effect of an ion was determined by calibrating the method in the presence and absence of the ion in question. Comparison of the graphs obtained revealed the type and magnitude of the interference.

Four types of interference are to be expected: —

(i) from ions which attack and destroy the complex, the reagent or both. Such are cerium, permanganate, peroxides and other oxidising agents.

(ii) from those ions which themselves form complexes with haematoxylin. Iron, chromium, tin, antimony, copper, zinc, bismuth[25] and some others fall into this class.

(iii) from ions which form complexes with fluoride ions, such as aluminium, iron, zirconium, vanadium (or vanadate), beryllium, some of which also fall in the previous class.

(iv) from ions forming strong complexes with aluminium. Oxalate and tartrate are the only ones we have tried which seem to fall into this class.

A full list of the interferences and their importances are given in Tables VII and VIII.

TABLE VII

THE EFFECT OF VARIOUS POSITIVE IONS ON THE DETERMINATION OF FLUORIDE WITH ALUMINIUM-HAEMATOXYLIN REAGENT

Ion	Concentration (p.p.m.)	Effect on fluoride determination	Nature of interference	Remarks
Na^+	2.3×10^3	Nil	None	
K^+	1×10^5	Nil	None	
Cu^{+2}	40	Marked loss of sensitivity	Itself complexes with haematoxylin	Removal essential
Ag^+	40			Removal essential as precipitates are formed with traces of Cl^- in reagents
Be^{+2}	40	Method fails	Complexes F^-	Removal essential
Mg^{+2}	40	Nil	None	
Ca^{+2}	4	Nil	None	
Ba^{+2}	60	Nil	None	
Zn^{+2}	4	Nil	None	
Cd^{+2}	4	Nil	None	
Hg^{+2}	40	Slight loss of sensitivity		Calibrate in presence of an equal amount of the ion

(Table VII, continued)

Ion	Concentration (p.p.m.)	Effect on fluoride determination	Nature of interference	Remarks
Al^{+3}				Removal essential since it upsets the proportion of Al in reagent and complexes F$^-$ without destroying reagent
Bi^{+3}	40	Method fails	Itself complexes with haematoxylin	Removal essential
La^{+3}	4	Nil	None	
Ce^{+4}	40	Method fails	Reagent destroyed by oxidation	Removal essential
Zr^{+4}	40	Method fails	Itself complexes with haematoxylin also with F$^-$	Removal essential
Sn^{+2}	4	Method fails	Itself complexes with haematoxylin	Removal essential
Pb^{+2}	4	Nil	None	
Cr^{+3}	4	Marked loss of sensitivity	Complex destroyed	Removal essential
UO$_2^{+2}$	30	Nil	None	
Mn^{+2}	4	Nil	None	
Fe^{+2} Fe^{+3}	4	Method fails	Itself complexes with haematoxylin	Removal essential
Co^{+2}	40	Nil	None	
Ni^{+2}	4	Nil	None	
Ru^{+3}	4	Marked loss of sensitivity	Itself complexes with haematoxylin	Removal essential

TABLE VIII

THE EFFECT OF NEGATIVE IONS IN THE DETERMINATION OF FLUORIDE WITH ALUMINIUM-HAEMATOXYLIN REAGENT

Ion	Concentration (p.p.m.)	Effect on fluoride determination	Nature of interference	Remarks
Arsenate Arsenite	40	Slight loss of sensitivity		Calibrate in presence of an equal amount of the ion or remove it.
Chloride	3×10^3	Nil	None	
Bromide	6×10^4	Nil	None	
Iodide	4	Nil	None	
Nitrate	1.5×10^5	Nil	None	
Nitrite	trace	Method fails	Destruction of reagent	Removal essential

References p. 368.

(Table VIII, continued)

Ion	Concentration (p.p.m.)	Effect on fluoride determination	Nature of interference	Remarks
Phosphate	4	Nil	None	
Sulphate	4.8×10^3	Nil	None	
Silicate	40	Marked loss of sensitivity		Removal essential
Dichromate	40		Destruction of reagent by oxidation	
Permanganate	40	Method fails	As for dichromate also colour of ion interferes	Removal essential
Perchlorate	<30	Nil	None	
Molybdate	40	Marked loss of sensitivity	Intensification of reagent colour	Removal essential
Vanadate	40	Marked loss of sensitivity	Reagent destroyed	Removal essential
Borate	40	Nil	None	
Formate	40	Nil	None	
Oxalate	4	Method fails	Destroys reagent by competing for Al.	Removal essential
Tartrate	40	Method fails	Destroys reagent by competing for Al.	Removal essential

3. DISCUSSION

The method is of general applicability to the determination of fluoride after separation from interfering ions by distillation as hydrofluosilicic acid. As here presented it is not suitable for the determination of fluoride in materials in which a volatile acid accompanies the fluoride on distillation *e.g.* from nitrates; the modifications necessary in such cases will be dealt with in a forthcoming paper.

Calculation of the standard deviation at several levels indicates that they are not significantly different and a mean standard deviation can therefore be calculated; this works out at between 1/4 and 1/3 μg. Thus taking three times the standard deviation to give a 99 per cent. probability then the limit of detection is just less than 1 μg in 25 ml of distillate. Since a distillate by the WILLARD AND WINTER technique normally has a volume of 150-175 ml this means that on a 10 g sample the limit of detection is of the order of 0.5 p.p.m. For work at lower levels a micro-distillation apparatus such as described by HORTON and his collaborators[26] enables the whole of the fluoride to be obtained in a distillate of 15-20 ml enabling the same limit to be obtained with one gram of material or a limit of the order of 0.05 p.p.m. on a ten gram sample.

The range over which the method has been used is 0-30 p.p.m. and in general the precision is better than ± 10% in many cases better than ± 5% and recoveries approach 100%.

The spectrophotometric finish presents distinct advantages over the thorium nitrate titration particularly since a less skilled operator is required.

As the manuscript of this paper was completed a paper giving details of a very similar method was published by PRICE AND WALKER[27]. This method employs the same principal as has been used by us but differs in a number of details and possesses neither the range nor so low a limit of detection. We cannot agree that the reaction: —

$$\text{Aluminium-haematoxylin lake} + 6F^- \rightarrow \text{haematoxylin } [AlF_6]^{-3}$$

represents what is taking place; the species formed is almost certainly $[AlF_2]^+$ and the lake does not decompose to give haematoxylin. We do not see the advantage of calibrating as per cent. transmittancy against fluoride concentration and feel that absorbancy (extinction) is preferable especially as under the proper conditions a straight line relationship can then be obtained. Under the heading of interferences Price and Walker quote only that caused by phosphate and sulphate whereas the ions likely to cause the most trouble are iron, aluminium, etc. We intend to discuss this work again more fully in Part III of the present series of papers.

We should like to place on record that the method described by ourselves has been used successfully in our laboratories since January, 1951.

4. ACKNOWLEDGEMENTS

The authors wish to thank Mr. D. G. BARRETT for determination of the interferences, and the Chief Scientist, British Ministry of Supply for permission to publish this paper.

SUMMARY

This paper describes a method for the spectrophotometric determination of fluoride. The fluoride is separated from interfering ions by the standard method of distillation as hydrofluosilicic acid. The fluoride in this distillate is determined by its destruction of the aluminium-haematoxylin complex; the amount of complex destroyed which is directly proportional to the concentration of fluoride is measured spectrophotometrically using radiation of 5700 A. The method will detect down to 0.05 p.p.m. of fluoride on a 10 gram sample with precision of rather better than ± 10% with larger amounts of fluoride.

RÉSUMÉ

On décrit une méthode de dosage de l'anion fluorhydrique. Le fluorure est séparé des ions gênants par distillation comme acide hydrofluosilicique. Le fluorure du distillat détruit le complexe aluminium-hématoxyline. La décoloration du réactif est proportionnelle à la concentration de l'ion fluorhydrique; on effectue cette détermination par spectrophotométrie (5700 A). La méthode permet de doser 0.05 p.p.m. de fluorure dans 10 g d'échantillon avec une précision meilleure que ± 10% pour les teneurs plus élevées.

ZUSAMMENFASSUNG

Diese Arbeit beschreibt eine spektrophotometrische Methode zur Bestimmung von Fluorid. Das Fluorid wird von störenden Ionen mit der Standardmethode, der Destillation als Siliciumfluorwasserstoffsäure, abgetrennt. Das Fluorid in diesem Destillat wird durch seine Zerstörung des Aluminium-Hämatoxylinkomplexes bestimmt. Die Menge des zerstörten Komplexes, die der Konzentration der Fluoride direkt proportional ist, wird spektrophotometrisch unter Benutzung einer Bestrahlung von 5700 A bestimmt. Die Methode weist noch 0.05 Teile Fluorid pro 1000000 in einer Probe von 10 g mit einer ± Genauigkeit nach, die bei grösseren Mengen Fluorid etwas mehr als ± 10% beträgt.

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α-PICOLINIC ACID AS A COLORIMETRIC REAGENT
I. DETERMINATION OF FERROUS ION

by

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In a previous communication MAJUMDAR AND SEN[1] observed that quinaldinic acid could be used for the colorimetric estimation of iron. An attempt has been made here to show that α-picolinic acid as a reagent can be better utilised as with iron (ous) it forms a highly stable complex in the presence of an alkali cyanide which, as may be suggested, besides giving the necessary alkalinity enters into the composition of the coloured complex.

The reagent α-picolinic acid prepared by the oxidation of α-picoline forms usually soluble salts with many bivalent and trivalent elements. Cobalt, nickel, copper, ferrous and chromic ions form coloured complexes. Of these ferrous complex is deeply coloured at pH 6-7 and becomes more so with the addition of alkali cyanide, which also increases the stability of the ferrous complex. Although the chromic complex forms a coloured system in acid solution on boiling for a few minutes with the reagent, the colour intensity does not vary proportionally with the concentration of the chromic ion. The ferrous complex on the other hand in the presence of cyanide obeys Beer's law from 0.08 p.p.m to 12 p.p.m. with a maximum absorption at 440 mμ. The cyanide though it intensifies the colour does not shift the absorption maximum, which also remains unaffected in the presence of an excess of the reagent or reducing agents, such as hydroxylamine hydrochloride, hydrazine sulphate, hydrogen sulphide, etc. With a cell of capacity 16 ml and thickness 20 mm, the optimum range with minimum relative error is found to be in the region of 1.6 to 8 p.p.m.

The alkali metals, magnesium, calcium, barium, strontium, silver, sulphate, nitrate, chloride, iodide, thiocyanate, salicylate, etc. have no effect on the colour system.

The ferrous complex with the reagent could not be isolated because of its high solubility in alcohol and in water, and hence the composition and the dissociation of the complex were elucidated by the method of JOB[2] and found to be $Fe(C_6H_4O_2N)_2$ with an average instability constant of $5 \cdot 10^{-5}$.

References p. 377.

EXPERIMENTAL

Apparatus and solutions

All transmittancy measurements were made with the Lumetron Model 402 EF of photovolt corporation with a cell of thickness 20 mm and capacity 16 ml, except during the study of the effect of the reagent, cyanide, reducing agent, ammonium carbonate and sodium acetate on the colour system and of the dissociation of the complex, where a Klett-Summerson photoelectric colorimeter with a tube cell of diam. 12 mm and capacity 15 ml was used.

In all studies very pure reagents were used. Solutions of iron were prepared from ferric nitrate with the addition of a few drops of nitric acid to keep the iron in solution. The amount of iron present in solution was determined both volumetrically and gravimetrically. Weaker solutions were prepared by dilution.

The reagent α-picolinic acid, m.p. 130-132° C, was obtained according to the method of RAMAGE AND CLEMO[3] by the oxidation of α-picoline supplied by Messrs British Drug Houses Ltd.

The effects of potassium cyanide, hydroxylamine hydrochloride and picolinic acid (Na-salt) on the colour system were studied with their solutions of different concentrations, while in other cases a 1% solution of sodium picolinate (1 g picolinic acid per 100 ml solution), 10% solution of potassium cyanide, 5% solution of hydroxylamine hydrochloride, 3% solution of hydrazine sulphate and a saturated solution of hydrogen sulphide at 30° C were used. Solutions of diverse ions were obtained from the nitrates, chlorides and sulphates of cations and from the sodium, potassium and ammonium salts of the anions.

Other solutions used were of caustic soda (10%), ammonium carbonate (5%) and sodium acetate (40%).

For the study of the composition and dissociation of the complex, solutions of Mohr's salt (acidified with sulphuric acid) and picolinic acid (Na-salt) of different molarities were utilised.

Colour reaction

The orange yellow coloured solution formed by ferrous iron in presence of reagent and cyanide has a maximum absorption in the region of 440 mμ. Excess of cyanide added after the addition of the reagent to the ferrous solution though intensifies the colour has no influence on the absorption maximum. Varying amounts of iron, reagent and reducing agents, such as, hydroxylamine hydrochloride, hydrazine sulphate and hydrogen sulphide show similar behaviour (*cf.* curves in Fig. 1).

The composition of ferrous picolinate as determined by JOB's[2] method shows that the complex is formed by iron with picolinic acid in the ratio of 1:2, *i.e.* of the formula $Fe(C_6H_4O_2N)_2$.

The ammonium carbonate and the sodium acetate are also found to increase the optical density owing to the complex, like the alkali cyanide, but the intensity of the colour developed by alkali cyanide is about three times that produced by ammonium carbonate and five times that by sodium acetate. Moreover, the optical density does not follow any linear relation with ferrous concentration when ammonium carbonate or sodium acetate is used to intensify the colour. Further the presence of an excess of sodium acetate or ammonium carbonate decomposes the complex. With alkali cyanide, on the other hand, the complex is rendered highly stable and does not decompose even on the addition of an excess of alkali. Thus it may be suggested that the ammonium carbonate or the sodium acetate simply gives the necessary alkalinity whereas the alkali cyanide besides providing the required alkalinity enters into the composition of the complex. A tentative formula for the compound may then be given as

$[Fe\,(C_6H_4O_2N)_2\,(CN)_2\,K_2]$ (*cf.* MAJUMDAR AND SEN[1])

Effect of the reagent, cyanide and reducing agents

The effect of picolinic acid, potassium cyanide and hydroxylamine hydrochloride on the colour system was studied at the wave length of maximum absorption, 440 mμ (Filter 44), varying the amounts of one of them while keeping the concentration of other two constant in a volume of 20 ml (*cf.* curves in Fig. 2). From the curves it appears that for maximum development of colour, the respective amounts of reagent, cyanide and hydroxylamine hydrochloride required are about 10, 100 and 40 times the amount of ferrous concentration and that they can

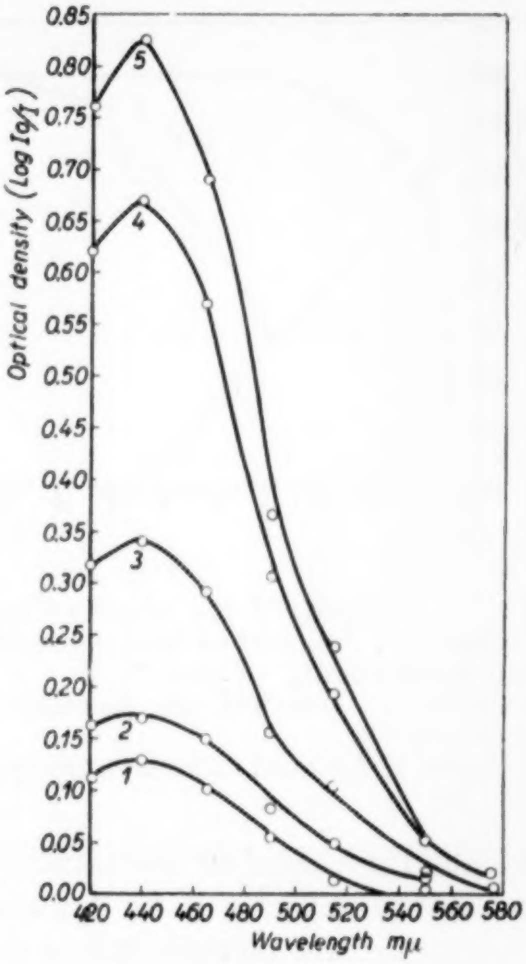

Fig. 1.

Study of the region of absorption maximum of ferrous iron-picolinic acid-cyanide system:

Curve 1. Soln.: iron = $2\cdot10^{-5}$ g; hydroxylamine hydrochloride = 1 ml; picolinic acid = 1 ml; potassium cyanide = 1 ml.

Curve 2. Soln.: iron = $4\cdot10^{-5}$ g; hydroxylamine hydrochloride = 1 ml; picolinic acid = 1 ml; potassium cyanide = 1 ml.

Curve 3. Soln.: iron = $8\cdot10^{-5}$ g; hydroxylamine hydrochloride = 1 ml; picolinic acid = 1 ml; potassium cyanide = 1 ml.

Curve 4. Soln.: iron = $1.6\cdot10^{-4}$; hydroxylamine hydrochloride = 1 ml (or H_2S water 5 ml or hydrazine sulphate 2 ml) picolinic acid = 1 ml; potassium cyanide = 1 ml.

Curve 5. Soln.: iron $2\cdot10^{-4}$ g; hydroxylamine hydrochloride = 1 ml; picolinic acid = 1 ml; potassium cyanide = 1 ml.

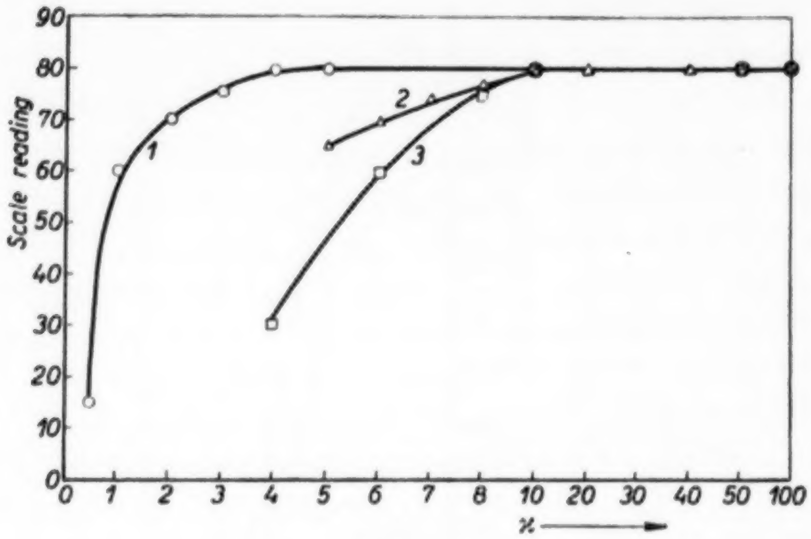

Fig. 2.
Study of the effect of reagents.
Curve 1. Amount of hydroxylamine hydrochloride (reducing agent) = $(x \cdot 10^{-3})$ g
Curve 2. Amount of picolinic acid (Na salt) = $(x \cdot 10^{-4})$ g
Curve 3. Amount of potassium cyanide = $(x \cdot 10^{-3})$ g

be tolerated even when present to the extent of 1000 times or over the amount of iron. The tolerance due to hydroxylamine hydrochloride may be increased to a very large extent if the amount of cyanide is increased to neutralise the acidity due to the hydrochloride.

For the reduction of iron, hydrazine sulphate or the hydrogen sulphide may as well be used.

Beer's law:

That the coloured system obeys Beer's law from 0.08 p.p.m to 12 p.p.m is evident from the fact that straight lines are obtained when the optical densities at 440 mμ (Filter 44), for a number of solutions with iron from 2×10^{-6} g to 3×10^{-4} g, are plotted against their respective concentrations. The procedure followed was to add solution of hydroxylamine hydrochloride or the hydrazine sulphate to the ferric solution to reduce the latter to the ferrous state. To this reduced solution were then added solutions of the reagent and the potassium cyanide in the order as stated and the volume made up to 25 ml with water. Every addition should be made with stirring, and the optical density of the coloured solution so prepared was then measured (*cf.* Figs. 3, 4, 5).

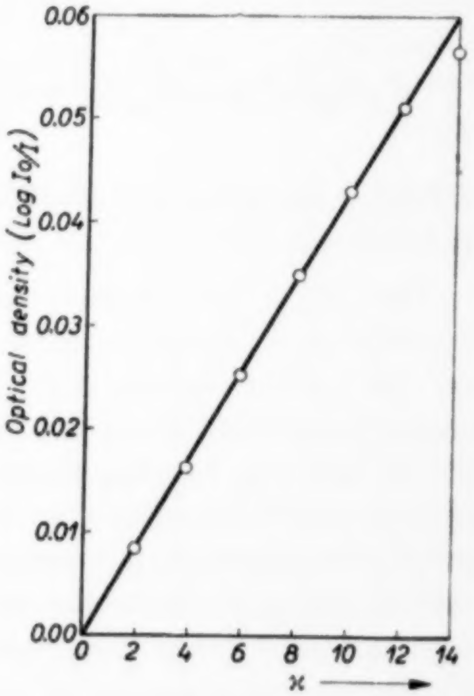

Fig. 3.
Study of Beer's law.
Amount of iron in 25 ml = $(x \cdot 10^{-6})$ g

Optimum Range: —

From the equation $\frac{dc}{c} = -\frac{dI}{I} \times \frac{0.434}{E}$ in which $E = \log \frac{Io}{I}$, the per cent. relative error $\left(\frac{dc}{c} \times 100\right)$ per one per cent. absolute photometric error has been calculated and plotted against transmittancy[4]. The way in which the analysis error varies with the transmittancy is shown in Table I and Fig. 6.

In order to define a suitable concentration range, per cent. absorbancy as ordinates has been plotted against logarithm of concentration as abscissas as proposed by RINGBOM[5]. The curve passes through an inflection as shown in the Fig. 7. The accuracy is greatest where the curve has its steepest slope — that is, when

$$\frac{dI}{\frac{dc}{c}} = \frac{dI}{2.303\, d \log c} = \max.$$

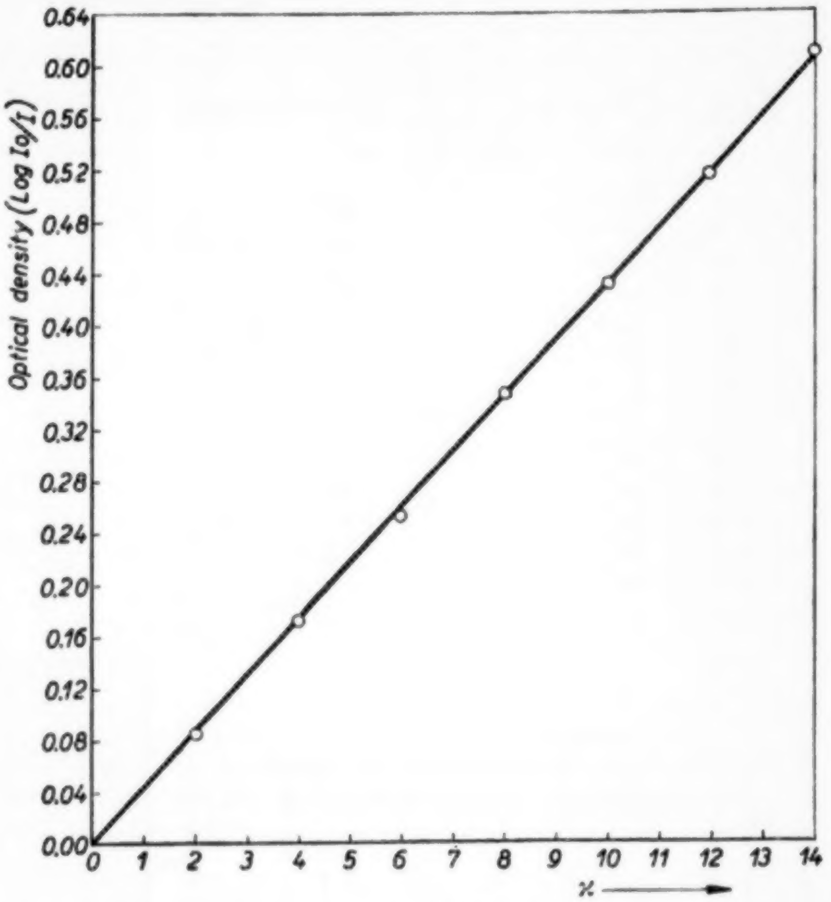

Fig. 4.
Study of Beer's law.
Amount of iron in 25 ml = $(x \cdot 10^{-5})$ g

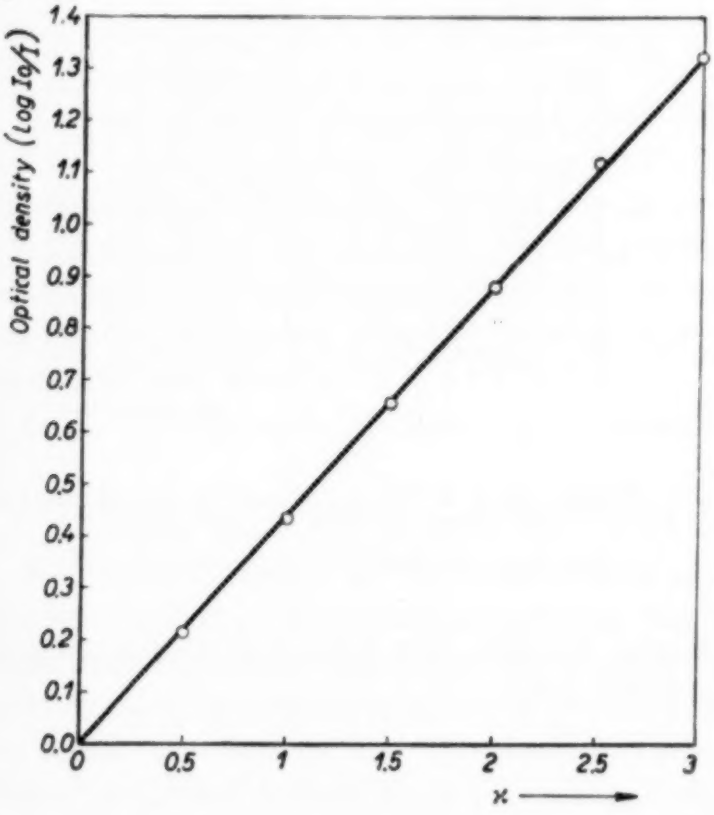

Fig. 5. Study of Beer's law.
Amount of iron in 25 ml = $(x \cdot 10^{-4})$ g

Thus the optimum range with the minimum error is in the region of 1.6 to 8 p.p.m of iron with a layer depth of 20 mm.

Stability of the colour

Full colour development is instantaneous after the cyanide addition and is independent of time interval between the additions of the reagents. The colour system is stable from 0° to 90° C and even on boiling the per cent. absorbancy remains unaffected. When the colour system with 0.1 mg iron and 1 ml each of hy-

TABLE I

Amt. of Iron g	% Transmittancy	$\frac{dc}{c}$ × 100 (p.c.) relative error per 1% photometric error
2×10^{-6}	98	49
6×10^{-6}	95	20.7
10×10^{-6}	90.5	11.05
20×10^{-6}	82.5	6.25
40×10^{-6}	67.5	3.74
60×10^{-6}	56	3.07
80×10^{-6}	45	2.8
100×10^{-6}	37	2.7
120×10^{-6}	30.5	2.8
150×10^{-6}	23	2.9
200×10^{-6}	13.5	3.7
250×10^{-6}	7.5	5.2
300×10^{-6}	4.5	6.8

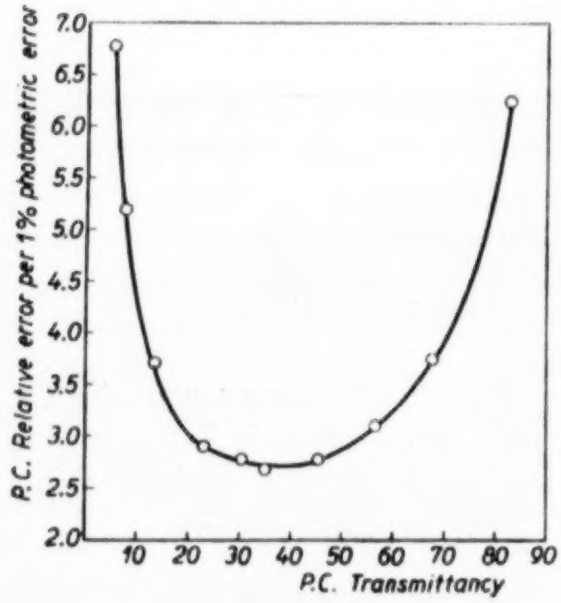

Fig. 6.
Evaluation of per cent. relative error (dc/c × 100) relative to 1%, absolute photometric error.

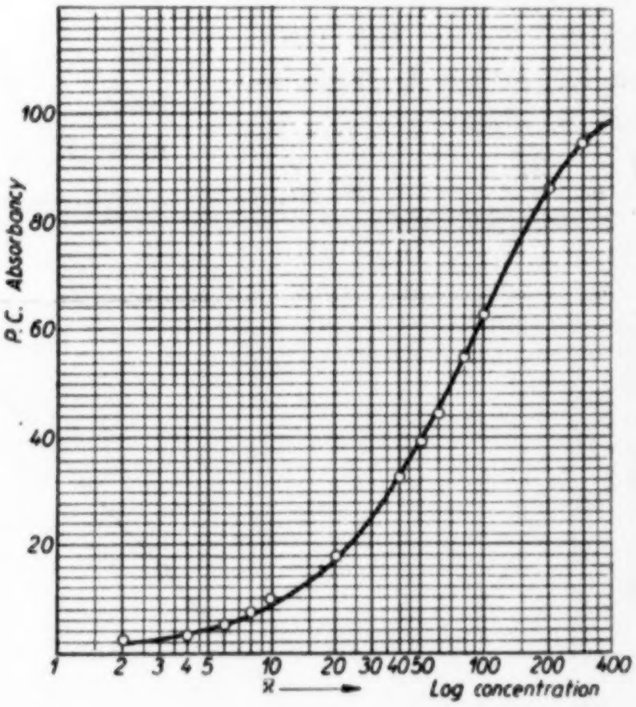

Fig. 7.
Evaluation of the optimum range of Beer's law with 20 mm layer depth.
Amount of iron in 25 ml = ($x \cdot 10^{-6}$) g

droxylamine hydrochloride, reagent and cyanide was kept well stoppered for about 110 days absorbancy remained the same.

Effect of diverse ions

The interference of ions was studied by measuring the colour intensity produced on the addition of the solution of ion under investigation to the solution of iron

TABLE II

Ions	Maximum amount of ion tolerated mg	Ion/Fe ratio at maximum toleration limit	Ions	Maximum amount of ion tolerated mg	Ion/Fe ratio at maximum toleration limit
Cu^{+2}	0.2	2	Th^{+4}	4	30(b)
Zn^{+2}	15	150	F^-	3	30
Zn^{+2}	60	600(a)	Oxalate	0.2	2
Mn^{+2}	3	30(b)	Tartrate	0.3	3
Mn^{+2}	3	30(a)	Citrate	0.5	5
Co^{+2}	0.2	2	WO_4^{-2}	0.5	5
Al^{+3}	5	50(a)	VO_3^-	1.25	12.5
Al^{+3}	50	500(d)	Benzoate	7	70
Ni^{+2}	20	200	PO_4^{-3}	0.03	0.3
Cd^{+2}	65	650(b)	Acetate	0.03	0.3
Pb^{+2}	8	80(b)	AsO_4^{-3}	0.1	1
Mo^{+6}	0.4	4	Formate	0.3	3
UO_2^{+2}	0.5	5	$B_4O_7^{-2}$	0.1	1
Be^{+2}	40	400(c)			

(a) The precipitate formed was dissolved with an excess of cyanide.
(b) The measurement was made with the filtrate.
(c) The precipitate was dissolved with alkali after full colour development.
(d) With excess of picolinic acid and cyanide.

(0.1 mg of iron) and then mixing with stirring 1 ml each of the hydroxylamine hydrochloride, reagent and the cyanide and making up the volume to 25 ml (*cf.* Table II).

The ions of silver, magnesium, calcium, barium, strontium, chloride, bromide, iodide, sulphate, nitrate, thiocyanate and salicylate are without any effect even when present to the extent of 100 mg in 25 ml. The silver chloride precipitate that is formed on the addition of hydroxylamine hydrochloride dissolves in excess of cyanide. The thiocyanate and the salicylate form with ferric ion coloured complexes, which are destroyed during reduction of iron with hydroxylamine hydrochloride.

Salts of chromium, chromate and dichromate should be absent.

Composition and dissociation of the complex ferrous picolinate

For the evaluation of the composition and dissociation of the complex, the absorption due to the mixtures (keeping the total volume constant) of equimolecular and non-equimolecular solutions (acidity of ferrous solution being $0.005M$ with respect to sulphuric acid) at 30-32° C was measured at 440 mμ (Filter 44) at which the ferrous and the sodium picolinate solutions had no absorption. The experimental data have been graphically represented in Figs. 8 and 9 by plotting the optical density or scale reading against the composition of the mixture.

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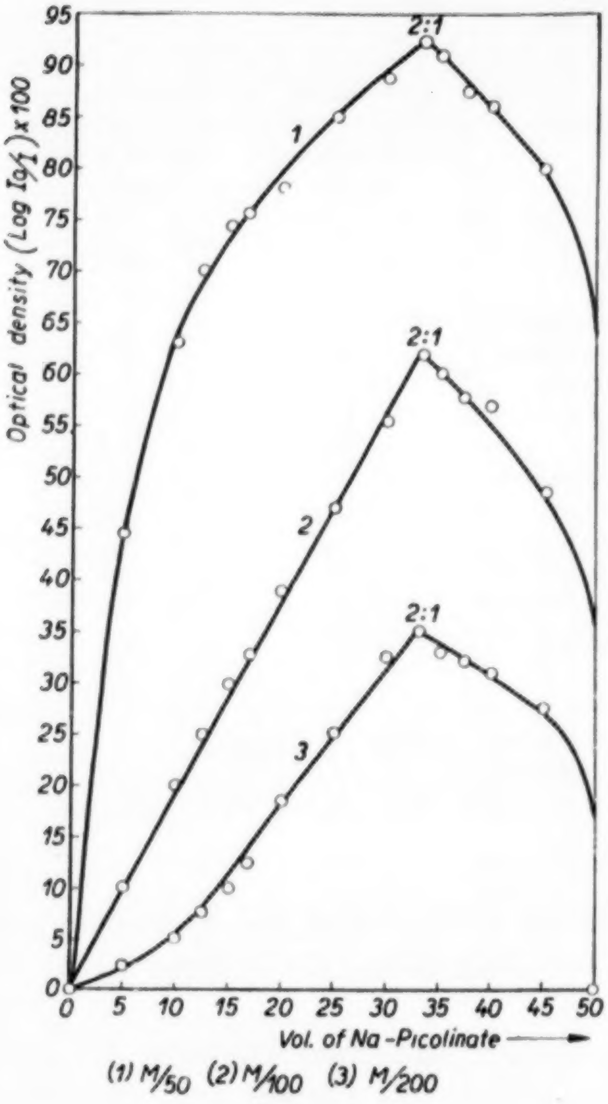

Fig. 8.

Optical density of the mixtures of equimolecular solutions.
Curve 1. $M/50$;
Curve 2. $M/100$;
Curve 3. $M/200$.

The density measurements of the mixtures of equimolecular solutions (*cf.* Fig. 8) lead definitely to the conclusion that the complex is formed between ferrous iron and picolinic acid when the reactants are in the ratio of 1:2 as the maximum is obtained at that ratio.

Now from the absorption data of the mixtures of non-equimolecular solutions the dissociation constant K can be calculated by applying the equation[2],

$$K = \frac{c^{(m+n-1)} \cdot p^{(n-1)} \left[(pm+n)x-n\right]^{m+n}}{m^{(n-1)} \cdot n^{(m-1)} \cdot (p-1)^{(m+n-1)} \cdot \left[n-(m+n)x\right]}$$

where m and n are the molecular ratios of iron and picolinic acid in the complex, c is the molar concentration of ferrous ammonium sulphate, pc the molar concentration of sodium picolinate, x ml of sodium picolinate solution combining with $(1\text{-}x)$ ml of ferrous ammonium sulphate to give the maximum effect.

The values of m and n being 1 and 2 respectively, the instability constant K is worked out by substituting the values of x, p and c in the above equation (*cf.* Table III).

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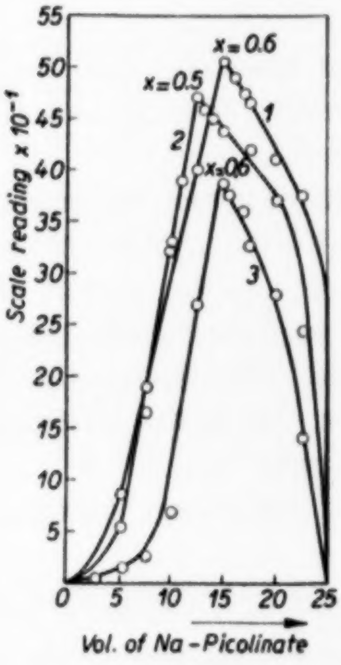

Fig. 9.

Optical density (scale reading) of mixtures of non-equimolecular solutions.
Curve 1. $M/100$ Ferrous solution and $M/50$ sodium picolinate.
Curve 2. $M/200$ Ferrous solution and $M/50$ sodium picolinate.
Curve 3. $M/300$ Ferrous solution and $M/100$ sodium picolinate.

TABLE III

Fig.	Curve	Conc. of ferrous ammon. sulphate soln.	Conc. of sod. picolinate soln.	x	p	Wave-length	K (instability constant) × 10^5
9	1	0.01	0.02	0.6	2	440 mμ	6.4
9	2	0.005	0.02	0.5	4	440 mμ	2.2
9	3	0.0033	0.01	0.6	3	440 mμ	4.08

Mean $K = 4.23 \cdot 10^{-5}$.

SUMMARY

α-Picolinic acid has been used as a reagent for the colorimetric estimation of ferrous ion. The transmittancy measurements show that iron from 0.08 p.p.m. to 12 p.p.m. may be easily determined with a cell of capacity 16 ml and thickness 20 mm. The effect of time, temperature and of diverse ions on the coloured system with an absorption maximum at 440 mμ have been critically examined. The optimum range with minimum relative error is found to be in the region of 1.6 to 8 p.p.m.

By JOB's method the composition of the ferrous complex, which is highly soluble and stable in water, is $Fe(C_6H_4O_2N)_2$ with a dissociation constant in the order of 10^{-5}.

RÉSUMÉ

L'acide α-picolinique a été employé comme réactif pour le dosage colorimétrique de Fe^{+2}. La méthode permet de doser facilement des teneurs en fer de 0.08 à 12 p.p.m. avec une cuve de 16 ml. L'effet du temps, de la température et de divers ions sur la coloration a été examiné. Le domaine d'utilisation optimum est compris entre 1.6 et 8 p.p.m. En appliquant la méthode de JOB, on a pu déterminer la composition de ce complexe du fer, très soluble et stable dans l'eau, $Fe(C_6H_4O_2N)_2$ (constante de dissociation environ 10^{-5}).

ZUSAMMENFASSUNG

α-Picolinsäure wurde als Reagens zur kolorimetrischen Bestimmung von Ferroionen benutzt. Mit dieser Methode kann man leicht Eisen in einer Konzentration von 0.08-12 $^{0}/_{00}$ in einer Zelle mit einem Fassungsvermögen von 16 ml und einer Dicke von 20 mm bestimmen. Der Einfluss der Zeit, der Temperatur und verschiedener anderer Ionen auf das gefärbte System mit einem Absorptionsmaximum bei 440 mμ wurde kritisch überprüft. Der optimale Bereich mit dem geringsten relativen Fehler wurde in dem Gebiet von 1.6-8 $^{0}/_{00}$ gefunden.

Die Zusammensetzung des Ferrokomplexes, der ausserordentlich gut löslich und stabil in Wasser ist, ist nach der JOB'schen Methode $Fe(C_6H_4O_2N)_2$ und besitzt eine Dissoziationskonstante in der Grössenordnung von 10^{-5}.

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α-PICOLINIC ACID AS A COLORIMETRIC REAGENT
II. DETERMINATION OF ALUMINIUM IN PRESENCE OF IRON AND CHROMIUM

by

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The problem for the determination of aluminium in the presence of iron has been approached from many directions[1]. Some preferred to free the aluminium from iron by extracting the ferric chloride with ethyl[2] or *iso*propyl[3] ether, the ferric thiocyanate with ethyl acetate[4] or amyl alcohol[5] or by removing the iron (III) cupferrate with a benzene-ether mixture[6], while, except BROPHY[7] who used mercury cathode for the removal of iron, most others precipitated out either of the constituents from solution. Caustic alkali[8], 8-oxine[9 10], trimethylamine[11] and cupferron[12] are used for the precipitation of iron, and hydrochloric acid-ether mixture[13], acetyl chloride[14] in acetone, *o*-phenetidine[15], succinic acid[16], thiosulphate[17], etc. are for the separation of aluminium. Of the organic bases, such as, aniline, pyridine and phenylhydrazine, the method[18] due to the latter as modified by ALLEN[19] and by GOLOWATY AND SSIDOROW[20] is being utilised by many workers as it gives an effective separation. Thioglycolic acid[21] and 2,2′-bipyridine[22] act as masking agents to keep the iron in solution in the ferrous state, while aluminium is precipitated as hydrated oxide by ammonium carbonate at a controlled pH.

For the separation from chromium the methods[23] used are mostly based on its oxidation to the hexavalent state by acid or alkali oxidising agents. Mercury cathode[7] may be also used to separate chromium. PINKUS[24], on the other hand, suggested the removal of aluminium from an acid solution by cupferron.

In Part I[25] it has been shown that α-picolinic acid can be used as a reagent for the colorimetric estimation of iron since it forms a highly stable complex in the presence of an alkali cyanide. The present paper discusses the use of the reagent as a masking agent for the separation of aluminium from iron (II) and chromium (III).

The ferrous picolinate complex is not decomposed by digestion with ammonium carbonate solution even at a pH as high as 7.7, and the chromic complex, which is formed from a weakly acid solution by boiling for a few minutes with the reagent α-picolinic acid solution, is stable up to pH 7.0. Thus aluminium can easily be precipitated from solutions of iron and chromium at an optimum pH between 6 and 7 by ammonium carbonate.

EXPERIMENTAL

Apparatus

pH measurements were made with a "Muir head" pH meter of type D-417.

Reagents

α-Picolinic acid solution: A 1% solution of the reagent was prepared from 1 g of the crystallised α-picolinic acid and 100 ml of water. In the same way as above, solutions of hydroxylamine hydrochloride (5%) and ammonium carbonate (5%) were obtained.

Other solutions used were (a) dilute ammonia, (b) dilute hydrochloric acid, (c) solution of bromocresol purple indicator and (d) ammonium chloride solution (2%) neutralised with dilute ammonia (methyl red indicator).

Standard solutions

Solutions of chromium and aluminium were prepared from their sulphates while the iron solution was from its chloride. They were kept in solution with the addition of required quantities of acids. The amounts of iron, chromium and aluminium present in their respective solutions were determined by standard methods from aliquots of their solutions.

All chemicals used for the experiments were of analytical quality.

RECOMMENDED PROCEDURE

Separation of aluminium from iron

The solution containing iron and aluminium was concentrated to about 10 ml and neutralised with dilute ammonia until a faint permanent precipitate formed, which was then dissolved in dilute hydrochloric acid. This solution was heated to boiling and treated with a few ml of the hydroxylamine hydrochloride solution till the solution became colourless owing to the complete reduction of iron to the ferrous state. After the reduction, a required amount of the reagent solution (α-picolinic acid at least six times the amount of iron present) was added to the solution and diluted to about 100 ml. The solution was again heated to boiling and to this was added ammonium carbonate solution dropwise with stirring till there was no further deepening of the colour due to the ferrous complex. The precipitate was then allowed to settle, filtered, washed with the ammonium chloride solution first by decantation and then on the filter to free it from iron, dried, taken in a weighed platinum crucible, incinerated, ignited to Al_2O_3 at about 1100° C and weighed after cooling in a dessicator with sulphuric acid. The first filtrate from the precipitate (before washing) was used for the measurement of pH. The results are given in Table I.

TABLE I

No.	Aluminium present. g	Iron present. g	Reagent added. ml	pH	Aluminium found. g
1	0.05280	0.005985	6	6.9	0.05270
2	0.02640	0.01197	60	6.6	0.02640
3	0.02640	0.02992	30	7.7	0.02635
4	0.02640	0.05985	35	6.5	0.02630
5	0.01212	0.005985	12	—	0.01217
6	0.01584	0.01795	10	5.78	0.01582
7	0.05280	0.01197	12	6.3	0.05280
8	0.01584	0.01046	60	6.5	0.01587

TABLE II

No.	Aluminium present. g	Iron present. g	Reagent added. ml	pH	Aluminium found. g
1	0.02640	0.01569	10	4.7	0.02466
2	0.02640	0.01569	10	4.85	0.02592
3	0.02640	0.01569	10	5.6	0.02608
4	0.02640	0.01569	10	5.8	0.02646
5	0.02640	0.01569	10	6.05	0.02646
6	0.02640	0.01569	10	6.2	0.02646
7	0.02640	0.01569	10	6.85	0.02640
8	0.02640	0.01569	10	7.6	0.02836
9	0.02640	0.01569	10	7.8	Too high
10	0.02640	0.01569	10	8.2	Too high

Study of the pH ranges

For the study of the optimum pH range for the effective separation of aluminium from iron, a few determinations were made with the procedure given above but with varying amounts of ammonium carbonate solution. In a few cases, a few ml of ammonium carbonate solution in excess of what was required for the maximum deepening of colour was added while in others a lesser amount of the ammonium carbonate solution was used. The optimum pH range with maximum intensity of colour was found to be between 5.8 and 6.85 (*cf.* Table II). During this investigation it was observed that with a greater amount of α-picolinic acid (about ten times the amount of iron) separation was possible at a little higher pH (7.7). (*cf.* Table III).

TABLE III

No.	Aluminium present. g	Iron present. g	Reagent added. ml	pH	Aluminium found. g
1	0.05280	0.005985	6	6.9	0.05270
2	0.02640	0.01197	15	7.6	0.02646
3	0.02640	0.01197	12	7.5	0.02656
4	0.02640	0.02992	30	7.7	0.02640
5	0.02640	0.05985	60	8.3	0.02741
6	0.02640	0.05985	60	8.4	0.02846

Separation of aluminium from chromium

To the acid solution containing chromium and aluminium was added α-picolinic acid solution (the amount of the reagent should be at least eleven times the amount of chromium present) and boiled for a few minutes (twenty minutes) till the green colour due to chromium was changed to red violet. The solution was then diluted, heated to boiling after the addition of a few drops of the bromocresol purple solution and treated with ammonium carbonate solution in the same way as referred above till the colour of the solution changed to bluish violet. The precipitate was then digested for a minute, allowed to settle, filtered, washed etc. as given above. The first filtrate was used for the pH measurement. (*cf.* Table IV). With larger amounts of chromium, the aluminium oxide precipitate was dissolved in dilute hydrochloric acid by warming and reprecipitated by ammonium carbonate in the presence of only 5 ml of α-picolonic acid solution.

The optimum pH for the separation of aluminium from chromium was determined, according to the method given for aluminium-iron mixture with excess or lesser amounts of ammonium carbonate required for the indicator change (*cf.* Table V), and found to range from 6.25 to 7.05.

TABLE IV

No.	Aluminium present. g	Chromium present. g	Reagent added. ml	pH	Aluminium found. g
1	0.02725	0.007475	10	6.7	0.02730
2	0.02725	0.01495	18	6.8	0.02741
3	0.05450	0.01495	18	6.7	0.05470
4	0.05450	0.007475	10	6.3	0.05450
5[a]	0.02725	0.03738	40	6.85	0.02730
6[a]	0.02725	0.07475	80	7	0.02741
7[a]	0.02725	0.04485	50	6.8	0.02730
8[a]	0.02725	0.05980	65	6.9	0.02730

[a] by double precipitation.

TABLE V

No.	Aluminium present. g	Chromium present. g	Reagent added. ml	pH	Aluminium found. g
1	0.02725	0.007475	10	5.4	0.01958
2	0.02725	0.007475	10	5.7	0.01968
3	0.02725	0.007475	10	5.9	0.02095
4	0.02725	0.007475	10	6.25	0.02730
5	0.02725	0.007475	10	6.7	0.02730
6	0.02725	0.007475	10	6.75	0.02720
7	0.02725	0.007475	10	7.05	0.02741
8	0.02725	0.007475	10	7.35	0.02762
9	0.02725	0.007475	10	7.6	0.02767
10	0.02725	0.007475	10	8.05	0.02825
11	0.05450	0.007475	10	6.3	0.05450

SUMMARY

Aluminium can easily be separated from solutions containing iron or chromium at an optimum pH of 5.8 to 6.85 for iron and at 6.25 to 7.05 for chromium, in the presence of an excess of α-picolinic acid, which acts as a masking agent for both. With larger amounts of chromium, reprecipitation is preferred to free the aluminium of chromium contamination.

RÉSUMÉ

On peut séparer facilement l'aluminium d'une solution contenant du fer et du chrome. En présence d'un excès d'acide α-picolinique (servant à masquer ces éléments), les pH optima pour le fer sont 5.8-6.85 et pour le chrome 6.25-7.05. En présence de fortes proportions de chrome, il faut procéder à une double précipitation.

ZUSAMMENFASSUNG

Aluminium kann leicht aus Lösungen, die Eisen oder Chrom enthalten, bei einem pH Optimum von 5.8-6.85 für Eisen und 6.25-7.05 für Chrom in Gegenwart eines Überschusses an α-Picolinsäure, welche beide Ionen maskiert, abgetrennt werden. Bei grösseren Mengen Chrom ist eine doppelte Umfällung vorzuziehen um das Aluminium von Chromverunreinigungen zu befreien.

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α-PICOLINIC ACID AS A COLORIMETRIC REAGENT III. DETERMINATION OF IRON AND ALUMINIUM

by

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In previous communications[1], Part I and II of this series, it was shown that α-picolinic acid could be used as a reagent for the colorimetric determination of iron from 0.08 p.p.m to 12 p.p.m in a cell of thickness 20 mm and capacity 16 ml and the optimum range with minimum relative error was in the region of 1.6 p.p.m. to 8 p.p.m. The experimental results were not influenced by the time, temperature, pH in the alkaline range, excess of reagent, cyanide and reducing agents, and the presence of numerous ions including aluminium (with excess of α-picolinic acid and alkali cyanide).

Other well known and most widely used methods for iron include thiocyanate[2], thioglycollate[3], 2,2′-bipyridyl[4] and 1,10-phenanthroline[5]. Some of the recent methods for the colorimetric determination of aluminium proposed from time to time are due to aluminon[6], alizarin[7], hematoxylin[8], eriochromecyanine R[9] and 8-oxine[10] (when extracted with chloroform). 8-oxine-chloroform extraction procedure is applicable over a pH of 4.5 to 11.5, except between 6.5 and 8 and then iron both in the bivalent and trivalent states interfered in acid and alkaline media[11]. There the iron interference was removed by converting it to ferrocyanide. In Part II was reported some other methods for the removal of iron before the determination of aluminium. Recently SPRAIN AND BANKS[12] utilised the reagent 1,10-phenanthroline as a complexing agent for iron to determine the iron spectrophotometrically and at the same time to remove its interfering effect from aluminium which was then extracted with a chloroform solution of 8-oxine. In view of the prohibitive cost[13] of the complexing agent, in this present investigation the reagent α-picolinic acid is used to complex iron in the presence of an excess of cyanide to keep the aluminium in solution and to measure the colour intensity due to iron. The aluminium is then determined from the same solution or from an aliquot of it by extracting the oxine complex with chloroform and measuring the absorbancy of the yellow colour of the tris (8-oxine) aluminium (III) in the chloroform solution.

EXPERIMENTAL

Apparatus

All transmittancy measurements were made with a Klett-Summerson photoelectric colorimeter, using a cell of 12 mm diam. and 15 ml capacity.

Reagents

Only reagent quality chemicals, as far as possible, were used.

α-picolinic acid solution: A 1% solution was prepared from re-crystallised α-picolinic acid of m.p. 130-132° C in 100 ml distilled water.

8-oxine solution: The chloroform though of reagent quality (Merck) was purified in the way suggested by GENTRY AND SHERRINGTON[11] and then washed with water and distilled and a 1% solution of 8-hydroxyquinoline in chloroform was prepared.

Other solutions used were a 5% solution of hydroxylamine hydrochloride in distilled water, a 10% solution of potassium cyanide in distilled water and a 0.01*N* acetic acid solution.

Standard solutions: Standard solutions in distilled water for aluminium and iron (III) were obtained from the respective sulphate and nitrate.

pH papers of British Drug Houses Ltd., were used to adjust the pH of the solutions.

RECOMMENDED PROCEDURE

To a solution containing different quantities of aluminium and iron were added 1 ml of the hydroxylamine hydrochloride solution to reduce the iron and then 1 ml each of the reagent α-picolinic acid and the cyanide with stirring in the order stated, and the volume of the solution was made up to 50 ml in a volumetric flask. Absorption measurements at 440 mμ (Filter 44) were carried out on a portion of the orange yellow coloured solution so prepared (*cf.* Part I of the series).

After the iron determination, a measured aliquot from the volumetric flask was taken in a separating funnel and treated with the acetic acid solution to adjust the pH of the aliquot to 4. 1 ml of the 8-oxine solution in chloroform was added to the solution followed by 5 ml portion of distilled chloroform. The contents were shaken for a few minutes, the excess pressure being released by removing the stopper. The two layers are allowed to separate and the chloroform layer is run in a stoppered flask containing a few grams (2 g) of fused calcium chloride. The extraction with the chloroform solution is repeated till the chloroform layer is colourless. After drying, the chloroform solution was made up to 50 ml with some extra chloroform and the optical density of the yellow coloured aluminium-oxine complex solution was measured at 400 mμ (Filter 40), using blank solution as the reference solution. Results are given in Table I.

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To calculate the results, the "calibration factor" was determined by measuring the transmittancy of a number of known solutions of iron and aluminium treated in the same way as described above. The scale readings of the unknown solutions were multiplied by the "calibration factor" for the concentrations of the known.

TABLE I

Iron present. µg	Aluminium present. µg	Iron found. µg	Aluminium found. µg
100	100	100	99
100	200	100	203
100	400	100	396
100	400	100	400
100	600	100	—
20	100	19	100
40	100	39	100
50	100	50	100
100	60	100	59
100	50	100	50
100	40	100	40
100	20	100	20

SUMMARY

A very simple, rapid and accurate method for the colorimetric estimation of micro amounts of iron and aluminium from the same solution has been described. The iron is determined in the ferrous state by its orange yellow colour with α-picolinic acid in the presence of an alkali cyanide, and aluminium concentration is measured from the yellow colour given by the chloroform solution of the aluminium-oxine complex after masking the effect due to iron by α-picolinic acid.

RÉSUMÉ

Une méthode de dosage colorimétrique très simple, rapide et précise, est décrite, permettant de déterminer Fe et Al dans la même solution. Le fer est dosé à l'état ferreux par l'acide α-picolinique, en présence de cyanure alcalin (coloration jaune orange) et l'aluminium par extraction du complexe aluminium-oxine dans le chloroforme (coloration jaune) après masquage du fer par l'acide α-picolinique.

ZUSAMMENFASSUNG

Es wurde eine sehr einfache schnelle und genaue Methode zur kolorimetrischen Bestimmung von Mikromengen Eisen und Aluminium in der gleichen Lösung beschrieben. Eisen wird als zweiwertiges Eisen durch die orangegelbe Farbe mit α-Picolinsäure in Gegenwart von Alkalicyanid bestimmt. Die Aluminiumkonzentration wird durch die gelbe Farbe bestimmt, die eine Chloroformlösung des Aluminiumoxinkomplexes nach dem Maskieren des Eisens mit α-Picolinsäure gibt.

References p. 387.

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SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Annual General Meeting

The seventy-ninth Annual General Meeting of the Society was held on Friday, March 6th, 1953, in the Meeting Room of the Chemical Society, Burlington House, London, W.1., with the President, Dr. J. R. NICHOLLS, C.B.E., F.R.I.C., in the Chair. The Financial Statement and the Report of the Council for the past year were submitted and approved. The membership of the Society was now 1592, an increase of 14 compared with the corresponding figure last year. The Society held six Ordinary Meetings during the year, five in London (one of which was organised for the Society by the Biological Methods Group) and one in Birmingham (organised for the Society by the Physical Methods Group); in addition, sixteen were held by the Society's Sections and Groups. The Society's journal, *The Analyst*, contained in its 1952 volume the record number of 1032 pages, which included 480 pages of the Proceedings of the First International Congress on Analytical Chemistry, held at Oxford, September 4th to 9th, 1952. The proceedings of the Congress would appear in book form in a few days' time.

The following Officers and Members of Council were elected for the forthcoming year — *President*: D. W. KENT-JONES, *Past Presidents serving on the Council:* Lewis EYNON, G. W. MONIER-WILLIAMS, J. R. NICHOLLS and George TAYLOR. *Vice-Presidents* : A. J. AMOS, T. McLACHLAN and Eric VOELCKER. *Honorary Treasurer* : J. H. HAMENCE. *Honorary Secretary* : K. A. WILLIAMS. *Other Members of Council* : C. A. ADAMS, N. L. ALLPORT, A. L. BACHARACH, R. C. CHIRNSIDE, B. S. COOPER, MISS M. CORNER, D. C. GARRATT, N. HERON, H. W. HODGSON, H. M. N. H. IRVING, H. E. MONK and H. C. S. DE WHALLEY.

Ex-officio Members : T. W. LOVETT (Chairman of the North of England Section), R. S. WATSON (Chairman of the Scottish Section), A. M. WARD (Chairman of the Microchemistry Group), J. HASLAM (Chairman of the Physical Methods Group) and H. O. J. COLLIER (Chairman of the Biological Methods Group).

In installing the President Elect in the Chair, Dr. NICHOLLS congratulated the members on their choice of one whose services to chemistry were so well known by his connection with the Royal Institute of Chemistry, as well as by his past services to the Society in many capacities.

The new President, Dr. KENT-JONES, then called upon the retiring president to deliver his Presidential Address.

Dr. J. R. NICHOLLS first briefly reviewed the progress of the Society. He referred to the inclusion in The Analyst of the Proceedings of the First International Congress on Analytical Chemistry held at Oxford last September ; credit for the record speed of publication was due to Mr. CHIRNSIDE, the Honorary Secretary of the Congress, and the Editorial staff of the Society.

The President's address was on the subject of *Public Health Hazards and the Analytical Chemist.* Whilst any legislative control to minimise such hazards must be founded on medical and pharmacological advice, it was the chemist who gave evidence to enforce such control. He summarised the conclusions given in the Fourth Annual Report of the Advisory Council (1950-1951, H. M. Stationery Office, Cmd. 8299) and put forward his views on implementing the policy there expressed. Public Health Hazards arose from pollution of the air with carbon dioxide and dust, leading to the formation of fogs; water hazards arising from the presence of trace elements; food hazards; clothing hazards; cosmetic hazards; and household hazards. Food hazards could be divided into metallic contamination, bacterial contamination, extraneous matter, wrapping materials, insecticidal residues and chemicals in food. In this last category, synthetic chemicals must not be regarded as necessarily more toxic than natural ones. Whilst there was no foreseeable difficulty with such relatively pure substances as anti-oxidants, emulsifying agents, antistaling agents and preservatives, the use of food colours was a problem. A list of prohibited colours was made over 25 years ago, and it could not be accepted that it listed all the harmful ones. Synthetic colours were usually made by coupling intermediates, some of which were known to be toxic. The effect of the possible breakdown of these colours in the body was not known. Another problem of recent development was the possible effect on the consumer of the use of drugs such as stilboestrol and antibiotics in the production of meat. Clothing hazards included the effect on the skin of dyes, moth-proofing agents and bleaching agents. Cosmetic hazards might arise through lack of control over their constituents, such as dyes. Household hazards arose from the use of detergents that were so efficient that little rinsing appeared necessary. The effect of these detergents, discharged with sewage to rivers, on water subsequently drawn for household use had also to be considered.

The control of public health hazards could be directed to the prevention of (i) hazards due to lack of hygiene (ii) hazards due to contamination, and (iii) hazards due to "chemicals" in the widest sense. Hazards due to lack of hygiene were preventable or minimised by proper hygiene, and there was adequate legislation to make this effective in the realm of public health. Reputable manufacturers' standards were generally higher than the prescribed minima, and education and common sense were sufficient safeguard in the household. Hazards due to contamination arose from the presence of traces unavoidable even in the best commercial practice. Statutory tolerances were appropriate, and existed for food. In this connection our Society played an essential part, as permissive tolerances had to be enforced and it was the chemist who developed methods of determining contaminants. Hazards due to chemicals could not be appropriately controlled by statutory tolerances: a chemical should either be permitted or forbidden.

It was necessary to review periodically any such control. This could only be achieved by a permanent body; the Poisons Board, in its field, was an example of such a body. An important problem was the hazard arising from the use of chemicals whose harmlessness had not been proved.

The standing committee should review the evidence for the use in food of any new chemical. The use of artificial sweeteners illustrated this point. Two such chemicals found favour in this country, saccharin and dulcin. Recent toxicological tests had shown saccharin to be completely harmless, but dulcin had harmful effects on different species of animals at certain concentrations and under specified conditions. This would justify such a standing committee banning the use of dulcin. Another sweetener, P 4000, had been advertised abroad as completely harmless to humans, but the tests were not disclosed. In more extended tests in the United States harmful effects were produced in animals, which showed the importance of prescribing the test conditions. The proposed standing committee would not permit the use of P 4000 in food until it had reviewed the results of adequate tests.

Another example was that of food colours. A subcommittee of the Food Standards Committee was considering this subject, but had not yet reported, and its conclusions could not be presumed. However, it was carrying out in a limited field the functions that the suggested standing committee should perform over the whole field. If such a committee prepared a list of permitted colours, it was important that chemical specifications should be given, as colours of lesser purity than that required for food colouring were often made for other purposes. If it was thought proper to protect the public more fully from the hazards that might arise from the use of harmful colours, a permitted list should be compiled from those colours now in use that have been adequately tested pharmacologically, and no new colour should be added until so tested and found satisfactory. Any colour on the list found harmful should be withdrawn at once, or after a specified time, according to the risk involved.

Colours in cosmetics would similarly be controlled; this should be acceptable to industry, which bears the ultimate civil liability for any hazards that might occur.

Anniversary Dinner

In the evening following the Annual General Meeting, a Dinner to celebrate the seventy-ninth anniversary of the Society was held, by kind permission of the Master, in the Hall of the Worshipful Society of Apothecaries of London, Blackfriars Lane, London, E.C. 4. The members and guests, numbering 100, were received by the President, Dr. J. R. NICHOLLS, C.B.E., F.R.I.C., and Mrs. NICHOLLS. The President afterwards took the Chair at the Dinner.

The guests of the Society and of the President included; — Dr. Charles HILL, M.A., M.D., D.P.H., LL.D., M.P.; H. W. CREMER, C.B.E., M.Sc., M.I. Chem. E., M. Inst. F., F.R.I.C. ; Norman C. WRIGHT, B.A., D.Sc., Ph.D., F.R.I.C., and Mrs. WRIGHT ; Stanley ROBSON, M. Sc., D.I.C., M.I. Chem. E., M.I.M.M., F.R.I.C., and Mrs. ROBSON ; G. ROCHE LYNCH, O.B.E., M.B., B.S., D.P.H., F.C.G.I., L.M.S. S.A., F.R.I.C. ; Sir E. John RUSSELL, O.B.E., D.Sc., F.R.S., and Lady RUSSELL ; The Hon. Mr. Justice LLOYD-JACOB and Lady LLOYD-JACOB; Mrs. S.B.R. DAVID, B.Sc., A.R.C.S., A.R.I.C. ; R. A. BECK ; J. LEE ; and the Clerk of the Worshipful Society of Apothecaries, E. BUSBY.

After the loyal toast had been honoured, the President, Dr. NICHOLLS, presented Bernard Dyer Memorial Medals to the first two Medallists, who had given the first two Bernard Dyer Memorial Lectures to the Society and were present as guests. He recalled that Bernard Dyer had been one of the original members of the Society, remaining a member for 73 years until his death in 1948. He was an agricultural chemist, which made it most appropriate that the first Memorial Lecturer should have been Sir E. John RUSSELL, who was also an agricultural chemist. The President then presented the Medal to Sir John.

Sir John RUSSELL, in thanking the President, said that he had happy memories of Bernard DYER, Chaston CHAPMAN and Augustus VOELCKER and had enjoyed a long connection with the Society.

Before presenting the second Medal to the Hon. Mr. Justice LLOYD-JACOB, the President said that the Bernard Dyer Memorial Medal had been designed by Mr. T. H. PAGET, who had been responsible for the obverse designs of the coins and medals of the reign of King George VI. He much regretted that Mr. PAGET had been unable to attend the dinner owing to illness. The President then presented the Medal to Mr. Justice LLOYD-JACOB, and said that it had been only chance that had turned him from chemistry to the legal profession.

The Hon. Mr. Justice LLOYD-JACOB, in thanking the President, said that he found himself in the position of a Junior following an eminent Leader, Sir John RUSSELL. His own connection with the Society was more recent, being with members who had given evidence in the court in which he sat.

Mr. H. W. CREMER, President of the Royal Institute of Chemistry, proposed the toast of the Society. He said that it was striking the number of members of the Society who were also Fellows or Associates of the Royal Institute of Chemistry. He complimented the Society, now in its eightieth year, on its growth; there were now many more members concerned with analysis of articles other than foods, and in the Subject Groups of the Society and in the topics chosen for lectures the Society's field had been widely extended of recent years. The Society had played a very full part in the Analytical Congress at Oxford in September, 1952. He paid tribute to the President elect, Dr. KENT-JONES, and said that on his becoming President the Royal Institute of Chemistry had lost a greatly honoured Honorary Treasurer. In that capacity Dr. KENT-JONES had shown great wisdom, sympathy and understanding. The Institute's Benevolent Fund had benefited enormously by the sympathy with which Dr. KENT-JONES sought to relieve those in distress. He wished the Society every success, and coupled his toast with the name of the President.

The President, Dr. NICHOLLS, in reply, thanked Mr. CREMER for his appreciative remarks about the Society. He, too, knew that the majority of the members of the Society were members of the Royal Institute of Chemistry. The Institute was a qualifying body, and as such might be described mathematically as the lowest common denominator of chemistry; if so, Analytical Chemistry was the greatest common measure in all other branches of chemistry.

Dr. A. J. **Amos**, in proposing the toast of the guests, said that it was fitting that he should refer first to Dr. Charles **Hill**. Chemists would recognise in him the phenomenon of allotropy — existence in several forms of one and the same body; first he was Secretary to the British Medical Association ,then the "Radio Doctor" and then he reappeared as the Parliamentary Secretary to the Ministry of Food. There had been a great deal of liaison between our Society and the Ministry of Food. Dr. **Hill**'s training, although in medicine, had been scientific so that he understood the analyst's language. The Ministry had in many ways earned the gratitude of the Food Industry. He was sorry that the Ministry's very valuable Advisory Service had ceased. Dr Norman **Wright**, Scientific Adviser to the Ministry of Food, had been a most successful Chairman of the Food Standards Committee, on which there was great scope for co-operation between the Ministry, the Food Trade and the Analyst. Dr. **Amos** welcomed Mr. **Cremer** both as Chemist and Engineer ; his Presidency of the Royal Institute of Chemistry was linked with his Past-Presidency of the Institution of Chemical Engineers — a record which he believed was unique. Dr. **Lampitt** represented the President of the Society of Chemical Industry ; the choice of him as proxy was very welcome, as he had been responsible for the formation of that Society's Food Group. Mr. Stanley **Robson**, the President of the Institution of Chemical Engineers, was also doubly welcome, for he was a Past-President of the Society of Chemical Industry. Dr. **Roche Lynch** representing the Master of the Worshipful Society of Apothecaries, was both host and guest, for he was the immediate Past Master of the Society of Apothecaries and a Past-President of the Society of Public Analysts. He was pleased to welcome the Bernard Dyer Memorial Medallists as guests; Sir John **Russell**'s outstanding contributions to analysis were well known, and Mr. Justice **Lloyd-Jacob** might well have been as eminent an analyst as he was a judge. Finally, but by no means least, he welcomed the ladies, without whose presence the dinner would not have been complete. The toast of the Guests was coupled with the name of Dr. Charles **Hill**.

Dr. Charles **Hill**, replying on behalf of the guests, said that he thanked the Society in general and the President in particular for the valuable co-operation they had extended to the Ministry of Food in the past 13 or 14 years. He understood Dr. **Amos**'s regret at the disappearance of the Advisory Service, but although as analysts they might be sorry that the Ministry's functions grew less in number, as ordinary citizens they might well hope for the speedy departure of the whole Ministry. He felt sure that the work of the Society would succeed just as well in the absence of the Ministry. The guests had appreciated and enjoyed the Society's hospitality.

The President, Dr. **Nicholls**, then invested Dr. **Kent-Jones** with the presidential badge and wished him success during his term of office. Dr. **Kent-Jones** expressed his thanks to the Society for the honour it had conferred upon him.

Ordinary meeting of the physical methods group

The Thirty-ninth Ordinary Meeting of the Physical Methods Group of the Society was held at 6.30 p.m. on Tuesday, March 3rd, 1953, in the Meeting Room of the Chemical Society, Burlington House, London W.1. Dr. J. **Haslam** was in the Chair and about fifty-five members and visitors were present.

The following papers on *absorptiometry* were presented and discussed :

The Use of High Absorbancy Reference Standards in Absorptiometry, by H. M. **Irving**, M.A., D. Phil., F.R.I.C.

Whenever the existence of a relationship between the concentration, C, of a solution and its transmittancy, T, or absorbancy (optical density), A, forms the basis of a determination of the former, experimental uncertainty in measuring T or A introduces an uncertainty in the result. The magnitude of the relative analytical error, $\triangle C/C$, is a function of T (or A). If the usual method of measuring the absorbancy of a sample against a "blank" or reference standard of pure solvent is adopted, the concentration range for maximum precision can be determined from the point of inflection of a plot of T against log C. Minimum error occurs when $A = 0.434$ ($T = 36.8$ per cent.), but there is no advantage in the device sometimes advocated of making known additions of material to that under investigation to bring the absorbancy up to this figure.

If, however, the reference standard of pure water is replaced by a solution of the substance under investigation, the measurement of relative transmittance (or differential absorbancy) still permits of a determination of sample concentration and the precision is considerably increased. Such use of high absorbancy reference standards has enabled absorptiometry to be applied to the analysis of copper, nickel, manganese and titanium alloys in which the named element is the major constituent, and their use can increase the precision of measurements involving two or more absorbing components.

The effects on precision of deviations from Beer's law, and of varying intensity of light sources, changes in slit widths, and other instrumental factors were considered in relation to the problem of determining the best experimental conditions for "Beckman-type" and other instruments in common use.

The Determination of Titanium by Precision Absorptiometry, by W. T. L. NEAL, M.A., A.R.I.C., and H. G. SHORT, M.Sc., A.R.I.C.

The titanium-hydrogen peroxide reaction has been used in the determination of titanium by precision absorptiometry with a Unicam SP500 spectrophotometer. The optimum concentration of reference solution has been determined by an experimental approach and the results obtained were presented in graphical form and discussed.

The effect and interrelation of various factors affecting the precision of the method (e.g., acid concentraton, temperature, etc.) have been examined. On the basis of these results a standard operating technique has been developed for the determination of titanium in titanium metal and titanium-oxygen alloys. This technique was described in detail, and the results obtained on a number of samples were given. The precision has been found to be better than one in a thousand.

The accuracy of course depends on the standard used for calibration. In the present work this was a sample of titanium metal of 99.92 per cent. purity, in which all known impurities had been directly determined.

A NEW REAGENT FOR STANNOUS TIN

by

J. R. A. ANDERSON AND J. L. GARNETT

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INTRODUCTION

The simultaneous nitration and sulphonation of β-naphthylamine having been carried out[1], it was decided to investigate the possible use of these products as developing reagents for cations in connection with partition chromatography on filter paper. It was found that one compound, 6-nitro-2-naphthylamine-8-sulphonic acid, was useful for this purpose. Forty-seven metallic ions were examined, and of these, only stannous tin gave an intense blue fluorescence when viewed under ultraviolet light.

EXPERIMENTAL

Spots of solution measuring 0.02 ml and containing approximately 0.2 mg of the metal ions were placed by means of a haemocytometer pipette on a sheet of filter paper (Munktell 20/150) and sprayed with a 2% aqueous solution of reagent. The sheets were air-dried for 15 minutes and viewed under ultraviolet light, any fluorescence being noted. The sheets were now sprayed with $15N$ NH_4OH, air dried, and again viewed under ultraviolet light, and the quenching of any previous fluorescence noted. The reagents employed are listed in Table I.

TABLE I

REAGENTS EMPLOYED FOR SPRAYING SPOTS OF METAL IONS

1. 2% aqueous solution of the ammonium salt of 6-nitro-2-naphthylamine-8-sulphonic acid.
2. 2% aqueous solution of the pyridine salt of 6-nitro-2-naphthylamine-8-sulphonic acid.
3. 2% aqueous solution of reagent No. 1 plus one per cent. of ethylene diamine.

The results obtained are shown in Table II.

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[1] A. BRYSON AND J. GARNETT, *Nature*, 171 (1953) 41.

TABLE II

RESULTS OBTAINED ON SPRAYING SPOTS OF METALLIC IONS WITH VARIOUS REAGENTS BEFORE AND AFTER QUENCHING OF FLUORESCENCE WITH NH_4OH

Metal Ion	Reagent No.					
	1		2		3	
	Before Quenching	After Quenching	Before Quenching	After Quenching	Before Quenching	After Quenching
Fe^{+2}						
Fe^{+3}	F		F		F	
Sn^{+2}	F	F	F	F	F	F
Sn^{+4}	F		F		F	
Hg^{+}						
Hg^{+2}	F		F		F	
As^{+3}					F	
As^{+5}						
Sb^{+3}					F	
Bi^{+3}					F	
Al^{+3}					F	
Cr^{+3}						
Mn^{+2}						
Zn^{+2}						
Sr^{+2}	F		F		F	
Ca^{+2}	F		F			
Ba^{+2}	F		F			
Mg^{+2}						
Cu^{+2}						
Co^{+2}	F		F			
Ni^{+2}						
Pb^{+2}	F		F		F	
Na^{+}						
K^{+}						
Rb^{+}						
Cs^{+}						
Li^{+}						
Ce^{+3}						
In^{+3}	F		F		F	
Mo^{+6}					F	
Pt^{+2}					F	
Au^{+3}	F		F		F	
Pd^{+2}	F		F		F	
Os^{+8}	F		F			
Tl^{+}						
Tl^{+3}	F		F		F	
W^{+6}	F (slight)	F (slight)				
Be^{+2}	F		F		F	
UO_2^{+2}						
VO^{+2}	F		F			
Th^{+4}			F		F	
ZrO_2^{+2}	F					
Ir^{+4}						

Metal Ion	Reagent No.					
	1		2		3	
	Before Quenching	After Quenching	Before Quenching	After Quenching	Before Quenching	After Quenching
Ru^{+4}	F		F		F	
Ti^{+4}	F	F (slight)	F	F (slight)	F	
Ti^{+3}	F	F	F	F	F	
Cd^{+2}						
Ag^{+}						

F = Fluoresces

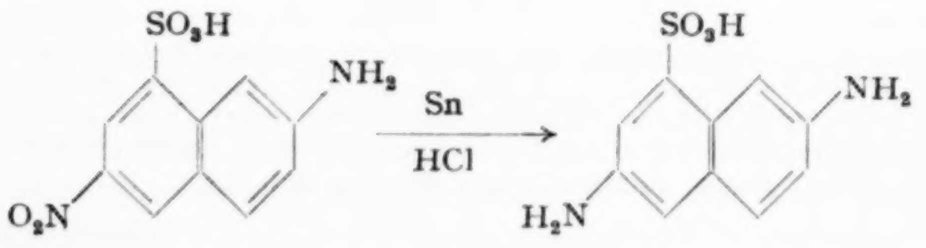
Sensitivity tests for stannous tin were carried out, 10 drops of 30% hypophosphorous acid being added per 100 ml of dilute stannous solution in order to prevent atmospheric oxidation. Spots containing 0.02 ml of the various dilute stannous chloride solutions were placed on sheets of filter paper, sprayed with 0.2% solutions of reagents numbers 1, 2 and 3 respectively and tested as previously described. It was found that reagent No. 3 was the least sensitive, but all three reagents were found to be capable of detecting one microgram of stannous tin.

Spots of reducing agents such as sodium sulphide, sodium metabisulphite, hydroxylamine and hypophosphorous acid were used in blank tests, and no fluorescence was observed under these conditions.

In additional experiments, it was shown that the fluorescence of stannous tin could be quenched by oxidation of the spots with hydrogen peroxide while treatment of non-fluorescent spots of stannic tin with hypophosphorous acid induced fluorescence.

DISCUSSION

The reduction of 6-nitro-2-naphthylamine-8-SO_3H in acid solution with stannous chloride proceeds as follows: —



The final product, *viz.*, 2,6-diamino-naphthalene-8-sulphonic acid, is obtained from the reaction mixture in the form of white scales of the chlorostannate complex. This complex is very stable, more so than the free acid, and exhibits an intensely blue fluorescence in aqueous alkaline solutions.

It appears likely that when the spot containing the stannous ion is sprayed with the above reagent No. 1, the powerful reducing action of the divalent tin converts the nitronaphthylamine sulphonic acid into a diamino naphthalene sulphonic acid, stabilising it as a chlorostannate complex which does not break down even under alkaline conditions.

The effect of such simple reducing agents as hypophosphorous acid, sodium metabisulphite, etc. can then be readily explained, since, in all probability, they do bring about reduction of the nitro group to the amine, but the corresponding diamino naphthalene sulphonic acid is most unstable and is readily oxidised under atmospheric conditions. This decomposition is accelerated in the presence of alkalis and would account for the quenching of fluorescence which has been noted with some cations when sprayed with NH_4OH.

In the case of some inorganic ions, such as Sb^{+3}, As^{+3}, etc. where fluorescence was obtained in acid conditions, then quenched under ammoniacal treatment, it is probable that the $[SbCl_6]^{-2}$ - etc. complexes are formed, but these are most unstable under the conditions of test and would certainly decompose when treated with NH_4OH.

SUMMARY

A new spot test for stannous tin has been evolved, using the ammonium salt of 6-nitro-2-naphthylamine-8-sulphonic acid as reagent, an intense blue fluorescence being produced under ultraviolet light. Of 47 metallic ions tested only Sn^{+2} fluoresced under the conditions of the test, as little as one microgram being capable of detection.

RÉSUMÉ

Une nouvelle réaction à la touche est proposée pour l'étain(II). On utilise comme réactif le sel d'ammonium de l'acide 6-nitro-2-naphtylamine-8-sulfonique; il se produit une fluorescence bleue intense en lumière ultraviolette. Des 47 ions métalliques essayés, seul Sn^{+2} donne une fluorescence dans les conditions de la réaction. On peut déceler jusqu'à 1 μg d'étain.

ZUSAMMENFASSUNG

Es wurde eine neue Tüpfelprobe für zweiwertiges Zinn entwickelt, welche 6-nitro-2-naphthylamin-8-sulfonsaures Ammonium als Reagens benutzt und im ultraviolettem Licht eine intensiv blaue Fluoreszenz zeigt. Von 47 untersuchten Metallionen ergab unter den Versuchsbedingungen nur Sn^{+2} eine Fluoreszenz, wobei noch ein Mikrogramm nachgewiesen werden konnte.

Received January 19th, 1953

THE WET ASHING OF ORGANIC MATTER EMPLOYING HOT CONCENTRATED PERCHLORIC ACID

THE LIQUID FIRE REACTION

by

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INTRODUCTION

The determination of traces of metal contaminants in the presence of large amounts of organic matter is habitually solved following a dry ashing procedure. An example is the determination of lead in such organisms as bone, liver, kidney or urine. The determination of the alkali metals, magnesium, phosphorus and other elements in hay, grain and feeds is another example. The estimation of copper in fish or oysters is a further illustration. The determination of small amounts of iron in leather formerly involved a dry ashing procedure. Many other illustrations could be cited.

All dry ashing procedures in the destruction of organic matter demand the use of rather large samples and a multiplicity of equipment. The electric muffles, platinum dishes, and other necessary apparatus, stamp these dry ashing procedures to be as troublesome as they are time-consuming.

The determination of chromium in chrom-tanned leather and medical catgut sutures serves to illustrate. A dry ashing procedure was formerly universally applied. In these cases chromium occurs in the 1-10 percentage range. A 1-3 g sample is sufficient for a macro-volumetric procedure. The dry ashing procedure retains the chromium in the residue from burning as acid insoluble chromic oxide. The dry ashing residue must be fused in a sodium carbonate-sodium peroxide flux in platinum. The chromic oxide of the ash is thus converted to sodium chromate. The ash fusion is dissolved in water and acid and the peroxide destroyed by boiling. The chromic acid thus formed may then be estimated by any of several common procedures.

Probably 50 per cent of the present production of leather involves the chrom-tanning process. The control laboratory for the tanning industry now employs a wet oxidation procedure exclusively of this determination of chromium in leather. The improved procedure involves the wet oxidation of the sample in hot concentrated perchloric acid. The chromium is simultaneously oxidized to chromic acid. The dissolution of the sample and the quantitative destruction of the organic matter requires 10-15 minutes. The excess oxidant (perchloric acid) need not be removed. Simple cooling and dilution only is required. The chromic acid is then estimated employing standard ferrous sulfate.

A tedious, complicated, formerly exclusively employed analyitcal procedure in the routine leather tanning control laboratory has thus been eliminated. It is replaced by a rapid, accurate, and universally accepted routine, perchloric acid wet ashing procedure[1].

The dissolution of samples of animal or vegetable origin by wet oxidation using perchloric acid in preparation for the determination of either metallic components or the non-metals sulfur and phorphorus, has been aptly designated *"The liquid fire reaction"*.

The dissolution of a sample of animal origin, such as liver, lung, kidney, hide, or bone, by oxidation using hot concentrated perchloric acid involves a complex series of reactions. Complicated organic structures are broken down into a series of fragments or degradation units. Each of these have characteristic reaction kinetics in contact with hot concentrated perchloric acid. The same type reaction mechanisms are involved in "the liquid fire reaction" as applied to samples of vegetable origin such as hay, grain, seeds, nuts, beans, wood, coal and many other products.

The study is here made of the oxidation of possible fragmentation degradation products of animal and vegetable origin using hot perchloric acid. Practical application of the procedure to a wide variety of natural products is subsequently described.

The oxidation of formic and oxalic acids by hot concentrated (70%) perchloric acid employing vanadium as catalyst. (Generalities)

Mixtures of glacial acetic acid and 70% perchloric acid have been subjected to boiling temperatures and no oxidation of acetic acid results. Instead the boiling of the mixed acids effects their separation. The lower boiling acetic acid is recovered unchanged in the distillate. This leaves, at 203° C, azeotropic compositioned perchloric acid of 72.5% strength. Thus the glacial acetic acid distillate may be condensed and recovered. There is no darkening of the hot mixed acids or other indication of a reaction of oxidation. There further is no indication that a perchloric acid-acetic acid azeotrope is formed. The separation of acetic acid from the boiling mixture is, however, slower than the individual boiling points of the two acids would indicate. This is because of the known compound formation between acetic acid and perchloric acid[2].

For propionic acid mixtures with perchloric acid essentially the same situation prevails. In this case, however, no known compound formation exists.

Acetic acid dissolved in 4 normal perchloric acid does not oxidize at a temperature of 55-70°C upon the addition of excess Ce(IV)[3], which condition provides an oxidation potential of 1.75 volts[4]. It is therefore clear that, since 70% perchloric acid at 180-200° C does not oxidize acetic acid, it requires a potential considerably greater than 1.75 volts to cause such oxidation reaction to occur (assuming that the oxidation reaction proceeds at a measurable rate).

The mechanism of the catalytic action of vanadium in the oxalic acid by hot concentrated (70%) perchloric acid.

The oxidation potential of vanadic acid according to the reaction, $VO_3^- + e^- + 4H^+ \rightarrow VO^{+2} + 2H_2O$, in strong acid solution has a value of approximately 1.45 volts. This value is exceeded in magnitude by 0.4 to 0.5 volts by hot concentrated (70%) perchloric acid. For this reason, if perchloric acid contains some organic material, such as oxalic acid, which may be easily oxidized by hot concentrated perchloric acid according to its reaction, $4HClO_4 + \triangle \rightarrow Cl_2 + 2H_2O + 2\text{-}O_2$, the reaction kinetics may be such that the oxidation of oxalic acid by vanadic acid is much more rapid. This will be conditioned upon the vanadate-vanadyl potential being high enough to oxidize the oxalic acid (or other oxidizable material which may be present). Provided, therefore, that the oxidation of V(IV) to V(V) is a more rapid reaction at a given temperature and concentration of perchloric acid than is the oxidation of the oxidizable material through perchloric acid, then a small quantity of vanadium will serve as catalyst for the given oxidation. Conditions thus described provide for the rapid reversal of the reaction, $VO_3^- + e^- + 4H^+ \longleftrightarrow VO^{+2} + 2H_2O$.

The same situation exists provided chromium is substituted for vanadium as catalyst. Here, however, there is an important limiting factor. The oxidation potential of the reaction $Cr_2O_7^{-2} + 6e^- + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O$ attains a value in strong mineral acid solution of approximately 1.36 volts. Should this potential be too low to bring about the oxidation of a given material its use will be ineffective as catalyst and its addition fail to effect the reaction rate. In this case the reaction of oxidation will depend only on the oxidation potential of 70% perchloric acid at the temperature employed. The chromium oxidation from green chromic ion to orange dichromate is useful as an indicator proving the completion of the oxidation of any organic matter.

One valuable feature in the use of concentrated perchloric acid as oxidant at temperatures of 160-200° C is the tenacity with which it retains its available oxygen. In addition perchloric acid is hydrated and the loss of this water of hydration, when the 60-65% acid is heated gradually from 160° to 203°, does not go beyond nor exceed that of the azeotropic composition. Thus water is expelled slowly up to an acid composition of approximately 72.5% under ordinary atmospheric pressures. As the strong 60-65% perchloric acid is concentrated by boiling its oxidation potential increases slowly and stepwise. In other words the oxygen made available by its gradual decomposition to give chlorine and oxygen is controlled, and by regulation of the acid strength and by controlling its temperature, there may be adjusted a delicate balance between oxygen supply and demand. Such controlled oxidation reaction conditions are not provided by any other, widely applicable oxygen carrier, variable as desired by regulation of reaction temperature and reagent concentration.

The oxidation of oxalic acid by hot concentrated perchloric acid with vanadium catalysis

Hot 70% perchloric acid (20 ml) containing 4 mg of chromium (added as $K_2Cr_2O_7$) were heated to 195° in a 500 ml Vycor Erlenmeyer flask. The flask and contents were provided with a refluxing still head and fume eradicator as shown in Fig. 1 and maintained at 190-195° C by the electric hot plate shown in the reaction assembly. A sample of 5.00 grams of crystalline oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, was added and the time required for complete oxidation noted. The point of complete oxidation is indicated by the chromium added as indicator. The hot perchloric acid solution of oxalic acid reduces the Cr(VI) to Cr(III) and

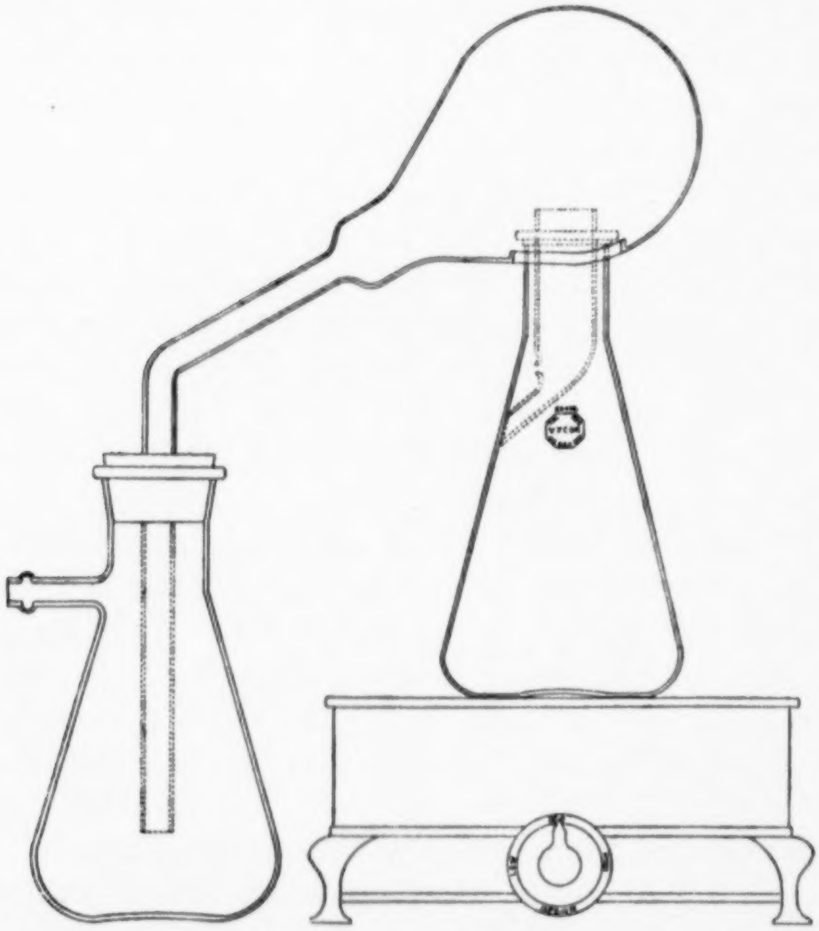

Fig. 1. Wet oxidation apparatus with refluxing still head and fume eradicator (aspirator bottle to serve as scrubber using dilute lye as absorbent).

the reaction solution is green. There is a brisk evaluation of CO_2 as the oxalic acid is oxidized and when this reaction is complete the Cr(III) rapidly oxidized to Cr(VI) with a color change from green to orange. The same reaction procedure is repeated with the addition of 0.15 to 0.75 mg of vanadium (added as saturated NH_4VO_3 dissolved in 70% perchloric acid) to serve as catalyst in reducing the time rate of oxidation. The results from a series of reactions are given in Table I.

TABLE I

THE OXIDATION OF OXALIC ACID BY 70% PERCHLORIC ACID AT 195-200° C WITH AND WITHOUT VANADIUM AS CATALYST

Oxalic acid taken 5.00 g, $H_2C_2O_4.2H_2O$. 20 ml 70% $HClO_4$. 10 mg $K_2Cr_2O_7$ employed as indicator. Vanadium added as NH_4VO_3 in 70% $HClO_4$. (0.1 ml = 0.15 mg V).

Vanadium added in mg	0.0	0.15	0.30	0.45	0.60	0.75
Reaction time in minutes	9.0	5.75	4.25	3.25	1.75	1.15

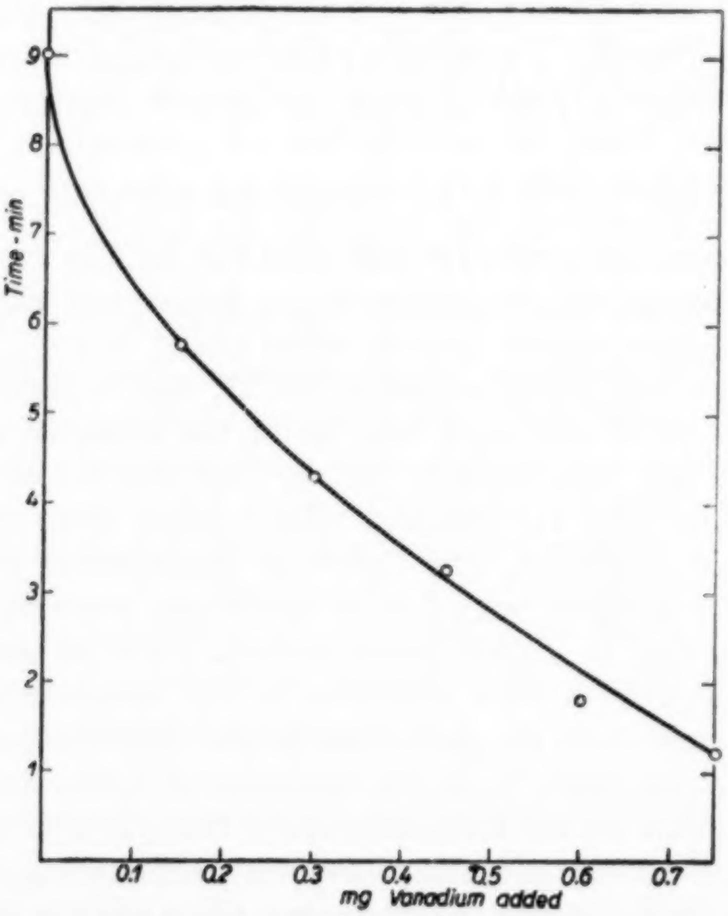

Fig. 2. Time rate of oxidation of $H_2C_2O_4 \cdot 2H_2O$ (5g) as catalyzed by vanadium.

The data of Table I are shown graphically in Fig. 2. The data of Table I indicate that the catalysis by vanadium is due to the instantaneous reaction of the vanadate-vanadyl couple, $VO_3^- + e^- + 4H^+ \longleftrightarrow VO^{+2} + 2H_2O$, in alternate directions. The reaction of the oxidation of oxalic acid by hot concentrated perchloric acid is not catalyzed by the Cr (VI)—Cr (III) couple as is shown by the fact that increased amounts of chromium do not alter the time interval of complete oxidation. Therefore, for the reactions of Table I chromium serves only as an indicator. The oxidation of oxalic acid from these facts requires a potential in excess of the Cr(VI)—Cr(III) couple but less than that of the V(V)-V(IV) couple. Since vanadium serves as catalyst the oxidation potential of hot 70-72% perchloric acid is sufficient to oxidize V(IV) to V(V) at an estimated potential of 1.8 to 1.95 volts, more rapidly, by far, than oxalic acid is oxidized by hot concentrated perchloric acid alone.

A hot perchloric acid solution of oxalic acid may be oxidized instantaneously by the addition of larger additions of vanadium than that indicated in the experiments of Table I.

The reactions of oxidation of oxalic acid by hot concentrated perchloric acid as catalyzed by vanadium are:

$$4\ HClO_4 + \triangle\ (195^\circ\ C) \rightarrow 2\ Cl_2 + 7\ O_2 + 2\ H_2O$$
$$14\ VO^{+2} + 8\ HClO_4 \rightarrow 4\ Cl_2 + 14\ VO_3^- + 4\ H_2O$$
$$C_2O_4^{-2} + 2\ VO_3^- + 2\ H^+ \rightarrow 2\ CO_2 + 2\ VO^{+2} + H_2O$$

The oxidation of formic acid by hot concentrated perchloric acid

Since hot concentrated perchloric acid does not oxidize acetic acid, it might be assumed that formic acid would likewise be unattacked. Such is not the case. A sample of crystalline sodium formate when added to 70% perchloric acid at 195° C results in its very rapid oxidation to CO_2 with a gush of gas evaluation.

For the purpose of estimating a time factor the reactants are best mixed at room temperature and then brought to 195°C on the hot plate. Chromium as indicator was again used. Its indicator effect differs from its reaction in the case of oxalic acid oxidation. The Cr(VI) is immediately reduced to Cr(III) which then forms a complex with formic acid which is colorless in low concentrations and faint blue in higher concentrations. After all uncomplexed formic acid has been destroyed a slow oxidation of the chromium-formate complex begins with the formation of the green chromic ion. This first formation of a green color indicates the practically complete oxidation of formic acid. Approximately 15 minutes is required for the formation of red chromic acid with the oxidation of the last trace of formic acid complexed with chromium.

Experimentally, 5 grams of anhydrous crystalline sodium formate was placed in a 500 ml Vycor Erlenmeyer flask and 20 mg of potassium dichromate added. After the addition of 20 ml of 70 percent perchloric acid, the flask and contents were placed on a 195° hot plate and allowed to react until the first green color appeared. The time required for the flask and contents to attain 195°C was found to be five minutes. At this point the reaction of oxidation becomes rapid as indicated by the rapid evolution of carbon dioxide. The reaction mixture, at first colorless, turns green in thirteen minutes of heating which marks completion of the oxidation except for the small amount of formate held to retarded oxidation in its complex with chromium.

A repetition of the test oxidation with the addition of 0.75 mg of vanadium as catalyst gave duplicate experimental results. Allowing five minutes heating interval to attain a reaction temperature of 195°, which marked the point at which the oxidation reaction was initiated, the time required for the oxidation to be completed is eight minutes. Neither vanadium nor chromium serves as a catalyst for this oxidation. The reaction temperature at the completion of the oxidation was found to be approximately 210° as a result of the accumulation sodium perchlorate from the sodium formate originally added.

From the fact that both formic and oxalic acids may be so readily oxidized and removed from solution by the use of hot concentrated solutions of perchloric acid, it would be predicted possible to determine acetic acid in the presence of the other two. The operation would involve carrying out the reaction of oxidation in an apparatus provided with a reflux condenser to prevent loss of acetic acid by volatilization and the subsequent determination of acetic acid. This would be accomplished, presumably, by the titration of acetic acid in the presence of perchloric acid. This titration of acetic acid with standard base (in which reaction perchloric acid[5] does not interfere), has been described.

The reaction between hot concentrated perchloric acid and formaldehyde

The reaction between hot concentrated (70%) perchloric acid and formaldehyde is very slow. Experimentally it would appear that such a combination upon boiling results in the separation of the formaldehyde by volatilization. Then upon heating to the boiling point for 4-5 minutes there is a resultant mild explosion. The destruction of formaldehyde by digestion of a mixture of concentrated perchloric acid and nitric acid is very rapid even at moderately elevated temperatures. Thus if formaldehyde should be a degradation product in "the liquid fire reaction" its formation involves no complications. Simply add nitric acid to destroy promptly any formaldehyde present.

The oxidation of tartaric acid by hot concentrated perchloric acid

A sample of ammonium tartrate weighing 1 g was added to a 20 ml sample of 70% perchloric acid in a 500 ml Vycor Erlenmeyer flask. A 20 mg portion of $K_2Cr_2O_7$ was added and the reactants heated from room temperature on a 195° hot plate. At 4 minutes the solution was green and at 8-10 minutes it was chocolate brown with evolution of CO_2. There was some carbon char formation. At 27 minutes the solution was green following its apparent complete oxidation. In 15 additional minutes the solution was orange color from CrO_3 formation.

Evidently the complex formation between the chromic ion and tartaric acid is very stable and slow to oxidize to CrO_3 as was the case with formic acid.

The reaction was repeated with the single modification that 1.5 mg of vanadium was added. At six minutes heating the solution turns straw colored and then chocolate brown in color. From 6-16 minutes CO_2 was evolved but no char resulted and the solution was green after all organic matter was destroyed. It required but 3 minutes continued heating until the solution was orange from CrO_3 formation.

Upon repeating the same conditions as just described with the addition of 2 ml of concentrated nitric acid it was found that at 4-6 minutes heating there was CO_2 evolution with little or no oxides of nitrogen being evolved and the solution was colorless. After 7 minutes the solution was green and all the organic matter was destroyed. At 15 minutes reaction time the solution was orange in color because of CrO_3 formation.

From these reactions it is seen that oxidation of tartaric acid by hot concentrated perchloric acid results in no violent reactions. Vanadium serves as an efficient catalyst in reducing the required oxidation time to half the period required in its absence also with the elimination of char formation. The best combination involves the use of vanadium as catalyst together with nitric acid to prevent the formation of dark brown degradation products and further reduce reaction time. The next experiment was made with the substitution of tartaric acid for ammonium tartrate.

A four gram sample of the crystalline tartaric acid was allowed to react with 20 ml of 70% perchloric acid to which was added 6 ml of concentrated nitric acid and 1.5 mg of vanadium as catalyst. At 195° C for 4 minutes no appreciable NO_2 was formed or CO_2 evolved and the solution was colorless. At 7 minutes NO_2 fumes were evolved and the solution was green. At 11.25 minutes an exothermic reaction set in with vigorous evolution of CO_2 and the solution was straw colored. At 11.5 minutes the exothermic reaction was at its maximum and there were copious white fumes from perchloric acid. At 11.75 minutes the solution turned orange from green due to CrO_3 formation and complete oxidation.

The oxidation of citric acid by hot concentrated perchloric acid

A sample of 1 g of citric acid was reacted as described above for tartaric acid. The reactants were 20 ml of 70% perchloric acid plus 20 mg of $K_2Cr_2O_7$ and 1.5 mg of vanadium. At 195° the solution was green in 4 minutes. CO_2 was being evolved at 6 minutes. At 10 minutes the solution was chocolate brown with one-half inch of foam from CO_2 evolution and there was some carbon deposited. At 15 minutes the solution was green and at 18 minutes the solution was orange owing to CrO_3 formation.

The oxidation reaction was twice repeated first with 1.5 mg of vanadium and again with 3.0 mg of vanadium. In each case 2 ml of concentrated nitric acid was also added. In both cases the reaction mixture was colorless with no NO_2 fumes. After 4 minutes the solution was still colorless, but NO_2 fumes and CO_2 evolution was brisk. After 5 minutes the solution was straw colored giving an exothermic activity with copious CO_2 evolution and it at once turned green. It required 20 additional minutes to bring about the CrO_3 oxidation.

From the last two experiments it is seen that nitric acid prevents the oxidation passing through the chocolate brown stage (partial carbonization or carmelization) and the presence of a small amount of vanadium speeds up the oxidation markedly.

A 4 g sample of citric acid was digested on a 195° hot plate in 20 ml of 70% perchloric acid with 10 ml of concentrated nitric acid. A 20 mg portion of $K_2Cr_2O_7$ was added together with 1.5 mg of vanadium. At 3.5 minutes there was no apparent oxidation and the solution was colorless. After 4 minutes reaction had just begun and the solution was straw colored from NO_2 and there was some CO_2 evolution. At 5 and at 6 minutes copious NO_2 fumes appeared and there was brisk evolution of CO_2 and the solution straw colored. At 7 minutes an accelerated exothermic reaction set in and at 10 minutes the solution was green and apparently all citric acid was destroyed. In an additional 11 minutes the CrO_3 formation resulted.

The influence of nitric acid as applied to the "liquid fire reaction"

In the case of the oxidation of oxalic, formic, citric and tartaric acids by digestion with hot concentrated perchloric acid as in the previous experiments, it has been shown that even though the organic materials have pronounced reduction potentials, no explosive reactions resulted. The oxidation potential provided by hot concentrated perchloric acid is known to be approximately 1.9 to 1.95 volts. Violent reactions would logically be predicted. The above-cited organic materials contain the carboxylic acid, methylene, and alcoholic OH groups.

Violent results may be encountered in oxidations involving hot concentrated perchloric acid.

This is for the reason that hot concentrated perchloric acid is a dehydrating agent. If ethyl alcohol is heated with concentrated perchloric acid, these dehydrating properties result in the esterification of the alcohol, ethyl perchlorate is formed and explosions result. Cellulose, sugars and polyhydric alcohols may be considered to be in the same category of reactants. None of these products are reactive with cold 72.5% perchloric acid. All, including cellulose, dissolve in 72.5% perchloric acid to give colorless solutions. Absolute ethyl alcohol may be mixed at ordinary temperatures with 72.5% perchloric acid without the least necessary apprehension. Pyrogallic acid dissolves in concentrated perchloric acid to give a colorless solution. This is not true in the case of nitric acid, both reactants at ordinary temperatures. In all these cases if the materials are in contact with hot concentrated perchloric acid explosions would certainly frequently result.

By what circumstance may "the liquid fire reaction" be applied with safety to the general destructive oxidation of organic materials?

An assurance involves the use of perchloric acid with the addition of nitric acid as a temporizing or damping reactant. By the use of nitric acid sugars, polyhydric alcohols, formaldehyde, and cellulose among other organic materials are readily oxidized and destroyed. Following the action of cold concentrated nitric acid, then the same reagent at rapidly rising temperatures, all readily oxidized organic matter is destroyed. The indicator for this oxidation is the evolution of copious fumes of brown oxide of nitrogen. When the reaction of nitric acid is complete, the high boiling, 60 to 72.5% perchloric acid, volatilizes and displaces the boiling nitric acid. With its elimination the 60% perchloric acid, upon further heating, concentrates slowly and progressively to the 72.5% water azeotrope. There is a steady stepwise increase in oxidation potential. All but the most difficultly oxidizable organic matter is thus more intensely reacted upon and destroyed. It is in this stepwise increase in oxidation potential that complex organic structures are broken up into fragmentation degradation products such as formic and oxalic acids. This fact accounts for their smooth rapid oxidation and elimination without carbonization and without violence of reaction.

The oxidation of cyclic ring nitrogen compounds

Such organic compounds as quinoline and other polycyclic ring nitrogen compounds are very resistant to destruction by oxidation in contact with hot concentrated perchloric acid. In case such materials are encountered several expedients apply effectively. Often the reaction of the destructive oxidation is catalyzed by the presence of a small amount of chromium or more effectively by the use of small additions of vanadium. In the determination of sulfur in coal following wet oxidation by hot mixed concentrated nitric and perchloric acids[6] use is made of the chromium or vanadium catalytic action. The oxidizing action may be made more intense by the use of mixed nitric, perchloric and sulfuric acids. In this application after the nitric acid has reacted at 140-150° and the excess is expelled, continued heating produces reaction potentials which continually increase first due to a steady increase in temperature and concentration of perchloric acid from 60 to 72.5%. Further heating then results in the formation of 80-100% perchloric acid in gradual stages. The accompanying gradual increase in oxidation potential provides for the destruction of the most stable aromatic nitrogen compounds. There is seldom need for such drastic treatment. The process is somewhat objectionable because of the formation of insoluble calcium sulfate. In the absence of sulfuric acid any calcium present remains in solution as calcium perchlorate.

The oxidation of sulfur by hot concentrated (72.5%) perchloric acid

Concentrated perchloric acid (the boiling water perchloric acid azeotrope, B.P. 203° C) oxidizes elemental sulfur smoothly and without hazard. If a sample of 1-2 grams of flowers of sulfur are added to a sample of 12-20 ml of boiling concentrated perchloric acid the sulfur melts and floats on the surface of the boiling acid. It is rapidly oxidized to volatile and gaseous sulfur compounds with but 25 % or less of the sulfur being retained as sulfuric acid by the reaction mixture. The reaction is not in the least hazardous.

The oxidation of organic compounds by the persulfate ion in warm dilute sulfuric acid as catalyzed by the presence of silver has been described[7] by FEIGL AND SCHÄFFER. In the decomposition of cupferrates, nickel dioximes, tannates, oxinates, methylene blue, and acid-base indicators among other organic materials, the organic matter is efficiently destroyed. By this process certain of the organometallic precipitates (such as Co(III)-α-nitroso-β-naphthalate) are not destroyed and in the case of the thio-compounds elemental sulfur is formed. By the perchloric acid decomposition of sulfur containing organic compounds no elemental sulfur can form and if the combination of hot concentrated perchloric acid with concentrated nitric acid is used as mixed oxidant, all the sulfur is retained after oxidation as sulfuric acid. This principle has been applied to the solution of copper sulfide ores as described by DIEHL AND SMITH[8]. In the use of nitric acid as solvent for this purpose there results an isolation of elemental sulfur which complicates the sulfide ore dissolution.

Hot concentrated perchloric acid oxidized phosphorus in its lower valence states to phosphoric acid or phosphate in the absence of nitric acid. The oxidized phosphorus is retained quantitatively. It may be precipitated as the "yellow precipitate" in the presence of perchloric acid without attendant complications.

PRACTICAL APPLICATIONS IN THE WET OXIDATION OF NATURALLY OCCURRING ORGANIC MATERIALS

Important previous applications of routine control analytical processes

The analysis of chrom tanned leather[1] and medical catgut for chromium[9] has been previously cited. Hundreds of thousands of such determination are probably applied annually in the tanning industries. The determination of sulfur in rubber is a much used nitric-perchloric acid wet oxidation[10, 11]. The determination of very small amounts of iron in wine accounts for probably 100,000 annual control analyzes following the wet oxidation of the sample containing alcohol, sugar and

TABLE II

THE OXIDATION OF OLIVE OIL, SPICES, NUTS, TEA AND COFFEE BY HOT MIXED NITRIC AND PERCHLORIC ACIDS WITH AND WITHOUT VANADIUM AS CATALYST

(10.0 ml of concentrated nitric acid Sp. Gr. 1.42 plus 15 ml of 70 % perchloric acid for each oxidation. Hot plate temperature 235° C — $K_2Cr_2O_7$ added = 20 mg — Digestion apparatus assembly as previously described.)

Sample Taken	Sample Wt. g	HNO_3 Reaction Interval min.	$HClO_4$ Reaction Interval min.	$HClO_4$ Reaction Color	Conversion Time Green, Cr^{+3} to Orange, Cr^{+6} min.	Vanadium Added mg	Remarks
Nutmeg	1.0	1- 5.5	5.5-16.0	Chocolate Brown	1.0	None	Smooth reaction of $HClO_4$ oxidation
Olive Oil	0.5	1- 9.5	7.5-16.5	,, ,,	10.0	None	HNO_3 reaction mild
Caraway Seed	3.0	1- 4.5	5.5-14.0	,, ,,	6.5	None	HNO_3 reaction intense
Pecan Nuts	3.0	1- 4.0	4.5-33.5	,, ,,	24.5	None	HNO_3 reaction intense
Pecan Nuts	3.0	1- 3.5	3.5- 7.5	,, ,,	4.5	9	Both acids react vigorously
Ground Mustard	3.0	1- 4.5	4.5-15.0	,, ,,	5.5	None	NHO_3 reaction mild
Ground Pepper*	1.0	1- 5.0	5.0-12.5	,, ,,	3.0	None	HNO_3 reaction intense
Ginger*	1.0	1-10.5	10.5-12.0	Olive Green	Indeterminate	None	HNO_3 reaction intense
Tea	3.0	1- 4.5	4.5- 9.0	Chocolate Brown	3.0	9	HNO_3 reaction intense
Cloves	3.0	1- 3.0	3.0- 7.0	,, ,,	3.0	9	HNO_3 reaction intense
Coffee*	3.0	1-12.0	12.5-20.0	,, ,,	7.5	None	HNO_3 reaction intense
Coffee**	3.0	1- 6.0	6.0- 9.5	,, ,,	1.5	9	HNO_3 reaction intense
Cinnamon	3.0	1- 4.0	4.5- 6.5	Olive Green	2.0	None	HNO_3 reaction color blood red. Both HNO_3 and $HClO_4$ react intense

* The addition of vanadium as catalyst without effect in a duplicate experiment.

** Nitric acid added 15 ml instead of 10.

other more difficultly oxidizable organic matter[12]. The analysis of feeds, hay, grain and alfalfa [13] for the determination of phosphorus, the alkali metals and magnesia is a very popular routine procedure. Many other examples could be cited.

Using the same apparatus previously described, the following products have been chosen to illustrate the multiplicity of practical wet oxidation ("liquid fire" oxidation procedures).

The oxidation of olive oil, spices, nuts, tea and coffee

The results from this series of wet oxidations are given in Table II.

The oxidation of proteins

Proteins in general constitute a large group of a general type occurring in meat, casein, albumin, keratin, haemoglobin, elastin and collagens. The "liquid fire reaction" as applied to the destruction of organic matter such as oysters, fish, cheese, eggs, bones, blood and hair fall in this category. The proteins contain 50-55% of carbon, 15-17.5% of nitrogen, 19-24% of oxygen, hydrogen 6.5-7.5% and up to 5% of sulfur and in some cases phosphorus. They contain a major portion of carbon as the carbonyl group and should be predicted to have smooth oxidation reactions with both hot concentrated nitric and perchloric acids. By this mixed acid digestion, the total sulfur and phosphorus content is retained as sulfuric and phosphoric acid together with any alkali or heavy metal contaminants, if present.

As a typical example of protein oxidation and mineralization a case of the destructive oxidation of the popular food stuff, dried beef, was selected for study. The results are given in tabular form in Table III.

From an examination of the data of Table III it may be seen that the hot nitric acid is capable of oxidizing much of the material but its destructive action leaves the major portion of the organic matter to be oxidized after the nitric acid has been dispelled from the reaction mixture. The perchloric acid reaction may be tempered by using a lower reaction temperature, using vanadium as catalyst, or best by the use of larger proportions of perchloric acid. By the use of larger quantities of perchloric acid the rate of increase in acid strength (and accompanying gradual increase in oxidation potential) as the acid concentration passes gradually from 68-70% and on up to the $HClO_4$-H_2O water azeotrope at 72.5% acid concentration, more time is allowed for the perchloric acid oxidation. These facts permit the stepwise oxidation of the more easily destroyed organic degradation products at the lower perchloric acid concentration and at lower required oxidation potential. The same damping effect may be had by addition of water for dilution of the perchloric acid concentration after the nitric acid reaction is complete. A convenient modification in apparatus for addition of

TABLE III

THE OXIDATION AND MINERALIZATION OF DRIED BEEF BY REACTION WITH HOT MIXED CONCENTRATED NITRIC AND PERCHLORIC ACIDS

(All tests included 20 mg of $K_2Cr_2O_7$ as indicator to denote complete oxidation of organic matter.)

Sample Wt. g	HNO_3 Sp. gr. 1.42 ml	70% $HClO_4$ ml	Vanadium Added mg	Hot Plate Temp. 0° C	Time of HNO_3 Reaction min.	Time of $HClO_4$ Reaction min.	$HClO_4$ Color Reaction	Remarks
5.0	10	15	9	235	8	9	Green	Vigorous HNO_3 reaction with much foaming. Exothermic $HClO_4$ reaction
10.0	10	15	None	215	15	16	Dark Brown	Same as above
10.0	10	15	9	235	3	4	Dark Brown	HNO_3 reaction vigorous with 2 inches foam. $HClO_4$ reaction exothermic with charring. Final reaction of $HClO_4$ caught fire.
10.0	22	15	9	235	4.5	5.5	Dark Brown	Same as above.
10.0	15	25	9	235	3.5	9.5	Dark Brown	Final $HClO_4$ reaction exothermic from dark brown to green to light brown with slight carbonization.
8.5	15	25	9	215	13.0	13.0	Dark Brown	Same as above. No char.

water or acid is shown in Fig. 3. By either the addition of a few more ml of concentrated nitric acid at the time the exothermic perchloric acid starts, or the addition of a few ml of water, there is an extension of reaction time. This retardation may have a beneficial effect in preventing the formation of dark colored organic degradation products which may otherwise be time consuming in their oxidation.

The results from the study of a list of protein materials is given in Table IV.

From the examination of the data in Table IV it will be observed that the variation in reaction conditions has a marked effect on the results. The variable factors include temperatures, ratio of mixed acids employed, and the presence or absence of vanadium as catalyst.

The best reaction conditions are those which result in a complete oxidation without the formation of dark organic reaction products which give to the reacting

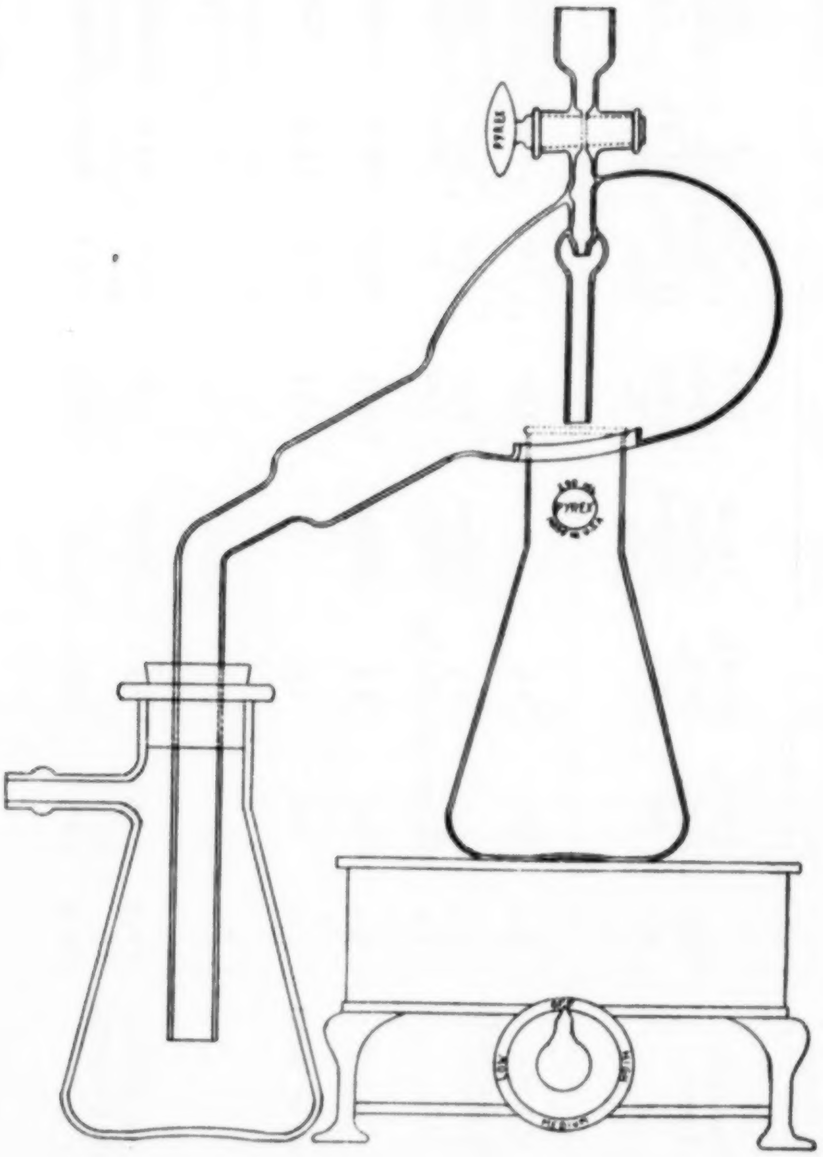

Fig. 3. Wet oxidation apparatus with modified fume eradicator tube.

References p. 421.

TABLE IV

THE OXIDATION OF ANIMAL PROTEIN BY HOT CONCENTRATED PERCHLORIC ACID OR ITS MIXTURE WITH CONCENTRATED NITRIC ACID WITH AND WITHOUT VANADIUM CATALYST

(20 mg of $K_2Cr_2O_7$ added to serve as indicator for the completion of oxidation)

Sample Type	Wt. g	HNO_3 67% ml	$HClO_4$ 70% ml	Vanadium Added mg	Hot Plate Temp. °C	Time of Reaction		$HClO_4$ Reaction Color	Remarks
						HNO_3 min.	$HClO_4$ min.		
Egg White (Hard Boiled)	5.0	10	15	9	235	3.0	6.5	Green	Smooth reaction throughout. No pronounced exothermic surge.
	5.0	10	15	None	230	7.0	32.0	Green	
	1.0	None	20 (60%)	None	210	—	38.0	Chocolate	Omission of HNO_3 modifies reaction unfavorably.
	5.0	10	15	None	235	10.0	17.0	Green	
Hippuric Acid	1.0	10	15	9	235	10.0	12.5	Green	Hippuric acid ($C_6H_5CONHCH_2COOH$) gives C_6H_5COOH and NH_2CH_2COOH upon acidification.
Salmon Fillet (Fresh Frozen)	12.5	15	15	None	230	12.0	23.0	Chocolate	Smooth vigorous reaction throughout.
	12.5	15	15	9	215	7.5	24.0	Chocolate	Final oxidation stage carbonizes then caught fire and burned fast.
	12.5	15	15	None	215	15.0	17.5	Chocolate	Exothermic reaction at 32.5 min. Color from brown to green sudden.
	12.5	30	15	None	215	32.0	88.0	Chocolate	Reaction time consuming but very smooth and temperature throughout.

Sample Type	Wt. g	HNO_3 67% ml	$HClO_4$ 70% ml	Vanadium Added mg	Hot Plate Temp. °C	Time of Reaction HNO_3 min.	Time of Reaction $HClO_4$ min.	$HClO_4$ Reaction Color	Remarks
Halibut Fillet (Fresh Frozen)	12.5	15	15	None	230	15.0	17.0	Chocolate	Smooth vigorous reaction throughout.
Gelatin	3.0	15	15	None	235	12.0	4.0	Chocolate	
	3.0	10	15	9	235	5.0	6.5	Green	Addition of vanadium very beneficial. Alters reaction type.
Casein	2.0	10	15	None	215	13.0	7.0	Chocolate	
	2.0	10	15	0.75	215	13.0	9.0	Green	Vanadium very beneficial. Reaction of $HClO_4$ gave no darkened products.
Oyster (Fresh)	10.0	10	15	None	215	12.0	16.0	Green	$HClO_4$ reaction exothermic.
Egg Yolk (Hard Boiled)	3.0	10	15	None	230	10.0	19.0	Chocolate	
	3.0	20	15	None	230	22.0	9.0	Chocolate	
	3.0	15	30	None	230	15.0	4.0	Chocolate	
	3.0	10	15	9	235	3.0	3.0	Chocolate	Vanadium very effective in oxidation of dark reaction products.
Wool Yarn	3.0	10	15	None	230	4.0	20.5	Green	HNO_3 and $HClO_4$ reaction exothermic.
	3.0	10	15	0.75	215	4.5	10.0	Chocolate	Vanadium speeds reaction at lower temperature.
Pork Rib Bone	3.0	10	15	None	230	8.5	27.6	Green	$HClO_4$ reaction exothermic at end of oxidation.
Fresh Shrimp	5.5	10	15	None	235	10.0	15.5	Chocolate	
	6.5	10	15	9	235	10.0	15.5	Chocolate	No catalytic effect from vanadium.

solution a dark chocolate color. It is to be preferred that the reaction color be either that of NO_2 (a straw color) or green from chromic ion. The destructive oxidation of casein is thus favorably modified by the addition of a small amount of vanadium (0.75 mg). The reaction is not only free from the formation of dark colored reaction products but the oxidation is complete in one-third less time.

The addition of vanadium catalyst may not only fail to prevent the formation of dark organic degradation products, but it may enhance this type reaction. An example is that of the oxidation of fresh salmon meat. In this case the presence of less than 10 mg of vanadium causes an otherwise quiet reaction to catch fire at the end of the reaction period and burn with much vigor. Attempts in this case to prevent the formation of dark reaction products failed if the reaction temperature was lowered or the ratio of nitric to perchloric acid increased.

In the case of the oxidation of boiled egg yolk the presence of vanadium as catalyst was very effective.

It may be said that the studies in the case of the destruction of organic matter by the "liquid fire reaction" were regulated to require short intervals of time with modest additions of oxidizing acids. Without doubt, the time, temperature, and reagent addition variables may bring more acceptable reaction conditions if desired. Conditions are preferable which shorten the oxidation time without undue increase in reaction intensity.

The oxidation of cellulose and similar type products

This type material includes the oxidation of hay, alfalfa, grain, tobacco, wood, straw and cotton. In general such products are destroyed to a major extent by hot concentrated nitric acid. If perchloric acid alone is employed for their complete oxidation, unless quantities are limited and the temperature kept moderate by the use of 60-65% perchloric acid, the reaction will probably be intense resulting in uncontrollable oxidation rates. Fortunately by the use of mixed concentrated nitric and perchloric acids, the reactions of oxidation are smoothly and progressively applied in such manner that no hazard is ever encountered. The mineralization of hay, grain, and animal feed for the determination of phosphorus, calcium, magnesium and the alkali metals is most speedily carried out by digestion by the "liquid fire reaction". As compared with the older process of dry ignition to destroy organic matter, the process is much more rapid and the total recovery of the mineral components and phosphorus more free from troublesome complications.

Some illustrative wet oxidations of this class of materials are given in the data of Table V. This type destructive oxidation of hay, alfalfa, and animal feeds, has been employed previously for example in the work of GIESEKING, SNIDER AND GETZ[13], and others.

TABLE V

THE OXIDATION OF CELLULOSE AND CELLULOSE PRODUCTS, GLYCEROL, AND SUGAR, USING HOT MIXED NITRIC AND PERCHLORIC ACIDS

(20 mg of $K_2Cr_2O_7$ added to serve as indicator of complete oxidation.)

Sample Type	Wt. g	HNO_3 67% ml	$HClO_4$ 70% ml	Vanadium Added mg	Hot Plate Temp. °C	Time of Reaction HNO_3 min.	Time of Reaction $HClO_4$ min.	$HClO_4$ Reaction Color	Remarks
Rhubarb (Dried)	5.0	10	15	None	235	9.5	23.5	Chocolate	Nitric acid action energetic.
	5.0	10	15	9	235	4.5	9.0	Green	Vanadium catalysis of oxalic acid oxidation evident here.
Tobacco	3.0	10	15	None	235	8.5	11.5	Light Brown	Some char formation due to $HClO_4$ oxidation.
	3.0	15	15	None	235	14.0	8.5	Light Brown	Char formation diminished.
	3.0	15	15	9	235	6.5	12.5	Green	No char formation.
Cellulose	1.0	10	15	None	230	5.0	12.0	Green	HNO_3 reaction predominates.
Glycerol	1.0	10	15	None	230	3.0	17.0	Colorless	Practically exclusively a nitric acid reaction.
Cane Sugar	1.0	10	15	None	230	5.0	17.0	Colorless	HNO_3 reaction predominates.
Dried Grass	3.0	10	15	None	230	8.0	19.5	Dark Brown	Both HNO_3 and $HClO_4$ reaction vigorous.

TABLE VI

THE LIQUID FIRE REACTION AS APPLIED TO ION EXCHANGE RESINS AND NYLON

(20 mg of $K_2Cr_2O_7$ added to serve as indicator of complete oxidation.)

Material Oxidized	Sample Weight g	67% HNO_3 ml	70% $HClO_4$ ml	Reaction Temp. °C	HNO_3 Effect min.	Time for Completion mm	$HClO_4$ Reaction Type	Remarks
Dowex 50	1.0	10	15	230	—	20	Colorless	No evolution of NO_2
IR-120	2.0	5	10	215	—	14	Dark Brown	NO_2 absent. Foaming from CO_2 evolution pronounced
Nylon	2.0	None	15	215	—	37	Colorless	Rapid initial CO_2 evolution
Nylon	2.0	10	15	215	10	38	Dark Brown	Rapid CO_2 evolution from both acid reactions

The destructive oxidation of Nylon and artificial exchange resins.

The results from these oxidations are given in Table VI.

Oxidation of motor car lubricating oil

The liquid fire reaction is applied with difficulty to the wet oxidation of organic material which does not dissolve in hot concentrated perchloric acid. Motor car lubricating oil is an example of this type material. Any destructive oxidation reaction must take place at the interface formed by the two immiscible liquids. The two reaction components are deprived of homogeneous, inter-acting, oxidation-reduction, electron exchange. In such case the sample to be oxidized frequently carbonizes extensively during contact with hot concentrated perchloric acid. The reaction resulting from this accumulation of finely divided carbon (and carmelized, semi-soluble carbonaceous degradation compounds), may accelerate, uncontrollably. A deflagration accompanied by a flash of fire of varying degrees of intensity may follow.

The use of chromium or vanadium as catalyst often serves to alter the course of the reaction materially. The carbonization reaction is modified in such manner as to form degradation products which are more easily oxidized. The reaction kinetics, thus altered, is frequently tempered, and violent interaction effectively retarded.

The addition of concentrated nitric acid to the reaction mixture is found to be most effective. The oxidation of the immiscible organic material is divided between the nitric acid oxidation (at 130-150° C) and the perchloric acid oxidation (at 150-203° C). The organic matter is thus progressively fractionated by acid attack from moderate nitric acid to intense perchloric acid oxidation. The gradual elevation of the temperature is an added reaction rate, controlling factor. The elimination of nitric acid from the boiling mixture results in a gradual elevation of temperature. The oxidation potential due to nitric acid increases accordingly. With the elimination of the nitric acid the perchloric acid reactivity sets in. Its oxidation potential increases as its concentration is augmented by rising temperature. The whole process is thus seen to be one of slowly increased reaction tempo with fractional destructive oxidation of the organic matter effectively controlled.

The determination of sulfur and of phosphorus in motor fuel oil is suggested following the destruction of organic matter by the liquid fire reaction. By the reaction of mixed nitric-perchloric acid, sulfur and phosphorus are oxidized to sulfuric and phosphoric acids. Perchloric acid does not interfere in the precipitation of either barium sulfate or the "yellow" phosphomolybdate precipitate if the determination of sulfur and phosphorus is desired.

The mineralization of motor car lubricating oil

The sample selected was number 20 grade motor car lubricating oil. The oxidant found best for its wet oxidation was a mixture of equal parts of 70% perchloric acid and 67% nitric acid. The temperature selected was a 200° C hot plate. The sample of fuel oil mineralized was approximately one gram for 40 ml of mixed oxidizing acids.

The reaction of oxidation is in two parts. From 140 to 152° C there is a steadily increased reaction tempo with a brisk evolution of NO_2 (from reduced nitric acid), accompanied by a rich lather-like foam surmounting the liquid reactants in the flask.

At a temperature of 152° C there was a recession of foam formation and fumes of perchloric acid suddenly appeared. The reaction at this point was exothermic and the boiling acid immediately turned from a straw color, due to NO_2, to colorless. A white, curdy, insoluble solid material separated at 15-17 minutes heating time and a faint deposition of black carbonaceous deposite sometimes formed which was immediately dispelled. The temperature increased rapidly from 152° to 198° at 15 to 18 minutes and the reaction was complete.

Repetition of the reaction a number of times gave practically identical results.

The use of 1 mg of vanadium as catalyst did not alter the results.

By carrying out the same reaction at a rate regulated by the hot plate temperature to require 2 hours for the complete reaction it is seen to follow three stages of oxidation. The first stage involves mainly reaction by nitric acid accompanied by the liberation of NO_2 with no fumes of perchloric acid. This reaction is complete when the NO_2 is no longer formed and foam production no longer results. The surface of the hot acid in the flask is coated with a colorless oil slick. The second stage of the reaction results in the oxidation of this oil slick to form first a curdy suspension which then oxidizes further forming an emulsion with the hot perchloric acid. As the temperature of the perchloric acid increases and its composition increases gradually to the azeotrope at 200-203°, the last trace of organic matter is oxidized and the boiling acid is colorless or slightly yellow due to formation of chlorine or chlorine oxides. From 15 to 16 ml of concentrated perchloric acid remained in the reaction flask after the reaction of oxidation was complete.

The general aspects of the oxidation are those of a distinctly fractional destruction of first the lower hydrocarbons, then a gradually increased destructive oxidation to leave paraffin type hydrocarbons. Finally, as the paraffin type hydrocarbons are destroyed, they form an emulsion with the boiling perchloric acid which converts a two phase system to essentially an emulsified homogeneous oxidation medium. The last stage of oxidation is smooth and devoid of carbonization although exothermic in kinetics.

An approximately 2 gram sample of No. 20 motor car lubricating oil was heated after addition of 20 ml of 70% perchloric acid only. The sample carbonized badly as the acid temperature reached the boiling point. Finally there was a flask of fire and the reaction mixture during 1 or 2 seconds had all the characteristics of a rocket fuel mixture. The reaction flask remained intact. The refluxing still head (Fig. 1) was ejected from the flask and the fume eradicator was broken. A black deposit of carbon remained to coat both the inside and outside of the reaction flask. An excess of perchloric acid was left in the reaction flask. Apparently most, if not all, the reactivity was in the gas phase rather than in the boiling acid. This phenomenon is obviously the result of reaction between hot vapors of perchloric acid as they passed through the supernatant layer of partially oxidized oil sample.

Tha analysis of fuel oil, and presumably crude oil, by oxidation with mixed nitric and sulfuric acid preparatory to the determination of metallic impurities is thus seen to be practical.

Perchloric acid explosion hysteria

Perchloric acid, beyond all reason, is one of the most feared reagents employed in widespread analytical applications. Perchloric acid on the other hand, in all justice to its scientific accomplishments, should be extolled for its remarkable virtue of exceptional stability. This is justified by examination of the above described experimental procedures.

The oxy-chlorine acids are four in number, hypochlorous, chlorous, chloric, and perchloric acids. Of these the first two are dealt with only in the form of their dilute aqueous solutions. The third (chloric acid) is never prepared in aqueous solutions stronger than 30% because beyond this strength the solutions explode. Only the last can be prepared and stored as the anhydrous, 100%, acid. A new method for its preparation, without apprehension of hazard, has just been described[14]. It is true that a bottle of anhydrous perchloric acid should be stored at very low temperatures to prevent slow, progressive, formation of accumulated decomposition products. Even at ordinary temperatures it may be stored for 20 to 30 days before spontaneous explosion results. The contact of anhydrous perchloric acid with wood, paper, rubber and other organic matter must of course be avoided.

The addition of one mol of water for each mol of anhydrous perchloric acid brings about a remarkable change. The melting point of the anhydrous acid (—112° C) is raised to +49.905° [15]. The crystalline monohydrate of perchloric acid (OH_2ClO_4) may be prepared in any quantity and stored for any extended period of time without the least decomposition or tendency towards explosive instability.

The addition of a second molecule of water to form the dihydrate ($OH_3ClO_4.H_2O$ or $O_2H_5ClO_4$ both the α and β forms being known) produces a material that has been shown to be a primary standard in acidimetry[16] and is a liquid at ordinary laboratory temperatures.

The concentration of dilute aqueous solutions of perchloric acid by heating, beyond 72.5% strength, cannot result at ordinary atmospheric pressures because of the formation of the perchloric acid-water azeotrope. Concentration by heating in vacuo (0-1 mm of mercury) does not permit increase in its strength beyond the dihydrate stage (73.605% $HClO_4$). These facts insure the limitation of acid concentration by heating, as in the above-described experiments, to concentrations which cannot, justifiably, be characterized as possible hazards.

Perchloric acid is now consumed to the amount of one hundred thousand pounds yearly of 70% concentration, as a conservative estimate, for application to "the liquid fire reaction". Its extended application to new analytical control procedures in industrial usage should be extended. The reactions studied as previously described were designed to proceed to completion at a rapid pace. By altering the reaction components and varying reaction temperatures the same ultimate results are possible at either an accelerated or retarded pace depending upon conditions.

SUMMARY

The wet ashing of a wide variety of organic compositions by the action of hot concentrated perchloric acid together with and without nitric acid and vanadium as catalyst has been described. These wet ashing procedures are known as "liquid fire reactions" because, although carried out at temperatures ranging from 100 to 235° C, organic matter is burned to carbon dioxide as completely as by dry ashing at high temperatures in electric heating muffles. The mineral components to be determined in the wet ashed samples are left in the excess of perchloric acid employed as oxygen donor and the often difficult dissolution of ash after the application of a dry ashing procedure is thus avoided. By the process as described the retention of sulfur and phosphorus is quantitative.

The study in detail has been made of the wet oxidation of a wide variety of natural products in 1 to 10 gram sample magnitudes. Apparatus design and reaction limitations have been described. Samples of carbohydrates, cellulose products, proteins and hydrocarbons in various natural organic products have been studied. The reaction mechanism has been postulated, the influence of vanadium as catalyst studied and temperature effects demonstrated. New analytical applications have been suggested.

RÉSUMÉ

L'auteur décrit une méthode de ,,minéralisation" pour un grand nombre de composés organiques, au moyen d'acide perchlorique, avec ou sans les catalyseurs, acide nitrique et vanadium. Ces procédés de minéralisation sont dits ,,liquid fire reactions", car ils s'effectuent à des températures comprises entre 100 et 235° C; la substance organique est transformée en anhydride carbonique, aussi quantitativement que par combustion sèche à hautes températures dans un four à mouffles électrique. Les composés minéraux à doser restent en solution dans l'excès d'acide perchlorique, (utilisé comme donneur d'oxygène); les difficultés de mise en solution sont ainsi évitées. Par ce procédé on retrouve quantitativement le soufre et le phosphore. Une étude systématique a été effectuée sur un grand nombre de composés variés (échantillon de 1 à 10 mg): hydrates de carbone, produits cellulosiques, protéines et hydrocarbures, dans différents produits naturels organiques. Le mécanisme de la réaction a été établi; l'influence du vanadium comme catalyseur a été étudié, ainsi que les effets de la température. De nouvelles applications analytiques sont proposées.

ZUSAMMENFASSUNG

Es wurde die Veraschung einer grossen Anzahl organischer Gemenge auf nassem Wege durch die Einwirkung von heisser konzentrierter Überchlorsäure zusammen mit oder ohne Salpetersäure und Vanadium als Katalysator beschrieben. Diese Verfahren der Veraschung auf nassem Wege sind als ,,flüssige Feuerreaktionen" bekannt, da, obwohl sie in einem Temperaturbereich zwischen 100 und 235° durchgeführt werden, organische Stoffe ebenso vollständig zu Kohlendioxyd verbrannt werden als bei Veraschungen auf trockenem Weg bei hohen Temperaturen in einem elektrisch geheiztem Muffelofen. Die in den auf nassem Wege veraschten Proben zu untersuchenden mineralischen Bestandteile bleiben in der als Sauerstofflieferanten benützten überschüssigen Überchlorsäure zurück und die oft schwierige Auflösung der bei der Anwendung der Veraschung auf trockenem Wege entstandenen Asche wird so vermieden. Schwefel und Phosphor werden bei dem so beschriebenen Prozess quantitativ zurückgehalten.

Im einzelnen wurde eine Untersuchung der Oxidation auf nassem Wege mit einer grossen Anzahl von Naturprodukten in Proben von 1-10 gr durchgeführt. Eine Zeichnung der Apparatur und die Begrenzungen der Reaktion wurden beschrieben. Es wurden Proben von Kohlehydraten, Zelluloseprodukten, Proteinen und Kohlenwasserstoffen in verschiedenen organischen Produkten untersucht. Der Reaktionsmechanismus wurde postuliert, der Einfluss von Vanadium als Katalysator untersucht und die Wirkung der Temperatur gezeigt. Es wurden neue analytische Anwendungen vorgeschlagen.

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THE NAPHTHORESORCINOL REACTION OF URONIC ACIDS*

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Interest in the uronic acids has been recently revived.

Compounds of this group were found in nature in various types of linkage and they were found to participate in the most varied biochemical processes[1]. Tollens and Rorive[2] recommended the significant color reaction with naphthoresorcinol (Nap) for identification of glucuronic acid. Mandel and Neuberg[3] have shown that the naphthoresorcinol reaction (Nap R) is not specific for glucuronic acid but that Nap will react by pigment formation with many carbonylic acids, including galacturonic acid (at that time still designated aldehydo mucic acid) and glyoxylic acid. Subsequently, these data were frequently used, confirmed and re-discovered[4]. In carrying out the reaction certain difficulties resulting from a simultaneous presence of sugars in addition to the uronic acids had to be eliminated. An excess of Nap should be added since the sugars will react with Nap under formation of condensation products that adsorb the uronic acid compound[5]. In this connection it was found that the extraction of the colored uronic acid derivative is more suitably[6] carried out by means of more selective solvents such as benzene, toluene, *p*-xylene, ethyl acetate, etc. than by means of the originally[2] used ether. This substitution of solvents proved superior[7], the inherent advantages having been stressed repeatedly[8] were more recently[9] described again. The working procedure according to Neuberg and Kobel[6], *i.e.* performance of the condensation of uronic acid with Nap on the boiling water bath and substitution of H_2SO_4 for HCl, seems most suitable[8]. According to this method the pigment is precipitated in fine readily soluble flakes and will not be resinous.

The pigment formerly considered as a derivative of xanthene or dinaphthylmethane[10, 11] is hydroxybinaphthylfurfurylmethane [12]. It was found at an early date and has recently been confirmed again[12] that furfural, which might be formed from the uronic acids, does not show the typical uronic acid color reaction[3, 5]. On the other hand, the behavior of the other compounds[13] obtained from the uronic acids by the effect of acids in addition to furfural is not known.

The data reported below will add to the knowledge of the naphthoresorcinol reaction. Close observers will have noticed that the shade of the pigment solution of the Nap R varies. This is attributable to an amount of hydroxylated substances contained in the solvent or the reaction medium. The pigment obtained from pure aldohexuronic acid appears reddish-violet, similar to diluted potassium permanganate solution, when dissolved in ether free of ethanol, ethyl acetate, benzene, toluene or xylene. Transitory mixed shades and finally steel or dark blue shades are obtained by the addition of methanol, ethanol, butanol, the pentanols, hexanols, tertiary amylalcohol, *n*-octyl alcohol, nonyl alcohol, 2,3-butyleneglycol, cyclohexanol, the methyl cyclohexanols, benzyl alcohol free of benzaldehyde, etc. The same effect may be obtained by trichloroethanol, trichlorobutanol, borneol, menthol, cholesterol, phenol, thymol, α-naphthol, linalaol, catechol when added either as solids or in benzene or ether solution to a reddish-violet solution of Nap R pigment. Typical conjugates of glucuronic acid compounds belong to this class of substances according to the above. Hence bluish shades* instead of the reddish-violet solutions are frequently obtained, if the Nap R is carried out on the uronides without elimination of the aglucuron, *e.g.* directly on urine.

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* Dedicated to Prof. Dr. Otto Loewi on his 80th birthday.

It has been known for a long time[5, 12] that the pigment of the Nap R dissolves with blue color in alcohols. The change of color from red to blue renders the reaction more distinctive since the blue shade is more intense. Accurate determinations may thus be carried out in an ordinary colorimeter. The following data were obtained by means of the Beckman spectrophotometer:

The maximum of optical density (transmission) at 570 mμ is practically identical for both types of pigment, whereas the course of the curves is obviously different. The spectrum of the blue solution shows a shift of the absorption band towards the red as compared to that of the violet solution.

As mentioned previously, benzene and toluene are excellent extraction agents for the pigment of the Nap R. Whereas well-known authors fully agree with us[7, 8] in considering this the best method, a divergent indication[14] was also encountered. Less satisfactory courses of reaction may be due to any of the following three reasons:

1. The previously mentioned adsorption of the Nap R pigment by typical impurities.
2. Unsuitable execution of the condensation: The pigment is precipitated in the form of a resin rather than as a finely dispersed flaky precipitate.
3. Excessive concentration of uronic acid. The quantity of pigment precipitated from a reaction medium containing more than 0.00088 g uronic acid per ml will dissolve with difficulty or incompletely when extracted with 5 ml toluene and somewhat more readily with 5 ml benzene. The quantity of pigment resulting from 0.00023 g uronic acid per ml will, however, dissolve readily in benzene as well as in toluene.

It has been attempted to accelerate completion of the Nap R catalytically. Tests with ceric sulfate as well as with $FeCl_3$ or $CuCl_2$ in quantities recommended for acceleration of the orcinol reaction[15, 16] yielded no conclusive results. In the case of uronides the required test period appears somewhat — if not substantially — shortened. The Nap R, exactly like the orcinol reaction, takes its course even without addition of an oxidant. (See also BISSET *et al.*[17] as well as MEYER *et al.* sub[8].)

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* Shift to the blue and intensification are also effected by acetic acid[6].

The statement that polyhydroxy acids will give a positive Nap R is erroneous. It has been previously[18] shown that the reaction is due to stubbornly adhering impurities. The latter are carbonylic acids which, according to general observations[19], are readily formed by oxidation of carbohydrates. Despite proof to the contrary this error persists in literature[20], especially with regard to mucic acid.

FISCHER AND HERTZ[21] reported at an early date on the difficulties of purifying mucic acid. In opposition to the mucic salts with inorganic bases, those with organic bases, *e.g.* with ethanolamine, diethanolamine, dimethylaminoethanol, pyridine, piperidine, morpholine, are readily soluble. According to our experience pure mucic acid is most suitably prepared by the following method: 4.2 g mucic acid are suspended in 200 ml H_2O and 3.6 ml morpholine are added. Solution is then obtained even at room temperature. After boiling with charcoal and subsequent filtration the mucic acid is precipitated with 22 ml M H_2SO_4. The crystallization starts almost immediately and is completed after 18 hours. The mucic acid filtered off by suction is snow white and does not show the Nap R. If necessary, the purification process via the morpholine salt is repeated.

It should be pointed out that in some instances a pseudo-positive reaction may be encountered. Owing to unknown reasons some of the commercial preparations of naphthoresorcinol as such contain traces of a substance which gives without addition of uronic acids a product soluble in benzene, toluene or ether with a yellowish-red color.

Also arabinose was erroneously reported[14] to give the Nap R.

Either the previously described phenomenon[22] of formation of a reddish suspension of the arabinose derivative in ether which might be mistaken for a solution was disregarded, or the arabinose was impure. The author[14] used D-arabinose which ordinarily is obtained by oxidative degradation of D-gluconic acid. A carbonylic acid (isomer of glucuronic acid) is obtained thereby[23].

SUMMARY

Sources of error are stated which should be considered in carrying out the Nap R with uronic acids. The most suitable conditions for quantitative evaluation of the reaction are specified.

RÉSUMÉ

Les auteurs signalent les causes d'erreurs possibles lors de la réaction de la naphtorésorcine avec les acides uroniques. Les conditions les plus favorables pour des résultats quantitatifs sont données.

ZUSAMMENFASSUNG

Fehlerquellen, auf die bei Anstellung der Naphthoresorcinreaktion mit Uronsäuren zu achten ist, werden dargelegt. Angegeben werden die besten Bedingungen für quantitative Auswertung der Reaktion.

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THE REACTION OF CARBOHYDRATES AND URONIC ACIDS WITH β-METHYLINDOLE

by

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Since first suggested in 1906[1], different methods and procedures were developed for color reactions of carbohydrates with indol and its derivatives as well as with related compounds of the pyrrole and carbazole groups. The reliability of these tests was found questionable according to BEILSTEIN[2], VAN DER HAAR[3] and MEYER[4].

MALOWAN's results[5] would have constituted an advance, had they been reproducible. This author stated that fructose and sorbose readily react with β-methyl indol (skatole) at room temperature in the presence of glacial acetic acid and concentrated hydrochloric acid, yielding a blue, chloroform-soluble pigment. Glucose was reported to react at 45° C only, while mannose and galactose were found not to react at all under these conditions. The author's claim that the color reaction could be obtained with glucuronic acid as well as with glucose, whereas no reaction had been obtained with galacturonic acid nor with galactose, is of interest in view of the following consideration:

The fact that ketohexoses react rapidly at room temperature while aldohexoses react slowly and on warming only is indicative of the reaction mechanism. The fact that aldoses, too, will react at higher temperatures was interpreted by MALOWAN on the basis of a catalytic transformation of aldoses into ketoses. Instead, the reaction seems to be due rather to the gradual formation of ω-hydroxymethylfurfural from the aldoses[6]. The role of ω-hydroxymethylfurfural in color reactions of sugars has been previously pointed out by various authors[7].

Obviously, ω-hydroxymethylfurfural can be formed from hexoses only:

$$C_6H_{12}O_6 = C_6H_6O_3 + 3\ H_2O.$$

It, therefore, seemed strange that glucuronic acid ($C_6H_{10}O_7$) reportedly showed the same color reaction as glucose, while galacturonic acid, its isomer, was supposedly characterized by the same absence of color reaction as galactose. Glucuronic acid cannot be transformed into ω-hydroxymethylfurfural, but only into furfural ($C_6H_{10}O_7 = C_5H_4O_2 + CO_2 + H_2O$). This in turn will not yield the above color reaction (see below).

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A possibility of differentiating between glucuronic and galacturonic acids would have been of interest in view of the fact that both of these acids occur in numerous natural products. However, differentiation between these two uronic acids according to MALOWAN could not be confirmed, nor could his differentiation between glucose, mannose and galactose be reproduced. All three of these isomeric aldohexoses will yield the same color reaction with β-methyl indole, with minor differences in the rate of reaction prevailing.

It should be added that no blue color reaction can be obtained in the case of mannurono lactone, which can be transformed into furfural only. The same applies to the isomeric aldohexuronic acids.

EXPERIMENTAL

Reagent: 0.3 g β-methyl indole, 3 ml glacial acetic acid, 7 ml conc. hydrochloric acid. 1 ml of the resulting fine suspension used for each experiment.

M/100 and *M*/1000 solutions of D-fructose, L-sorbose, D-glucose, D-mannose, D-galactose, D-glucuronic acid lactone, D-galacturonic acid, D-mannuronic acid lactone, L-arabinose, D-lyxose, D-ribose, D-xylose, L-fucose, L-rhamnose, D-gluco-D-gulo-heptose, D-gluco-D-sorbo-heptose. One ml of the reagent was mixed with 1 ml of the equimolar carbohydrate solutions.

The solutions of glucose, mannose and galactose react negligibly at room temperature, whereas glucose and mannose on warming produce a color reaction of practically the same intensity as that of fructose obtained at room temperature. Galactose reacts more slowly. The three uronic acids do not react with β-methyl indole at room temperature, on warming they turn olive, but do not produce a blue pigment extractable by chloroform. Furfural and the pentoses arabinose, lyxose, ribose and xylose, which at the prevailing test conditions produce furfural, react in the same way. Gluco-gulo-heptose reacts at room temperature only slightly, but on warming a brown precipitate is formed which dissolves in chloroform giving a violet color. Gluco-sorbo-heptose behaves likewise. The methylpentoses fucose and rhamnose produce a reddish-brown precipitate when warmed with β-methyl indole. This precipitate is soluble in chloroform giving a raspberry color, characteristic of α-methylfurfural. ω-Hydroxymethylfurfural* as well as hexoses yield a blue pigment. ω-hydroxymethylfurfural, furfural and α-methylfurfural even in very diluted solutions react more rapidly than the carbohydrates or uronic acids from which they had been formed.

SUMMARY

Aldo- and keto-hexoses produce with β-methylindole a pigment that is soluble with blue color in chloroform. The same applies to ω-hydroxymethylfurfural. Pentoses and uronic acids as well as furfural produce an olive color reaction, but no blue soluble pigment. Methylpentoses and methylfurfural produce a red pigment, the chloroform extract of which is of raspberry color. The behavior of the heptoses is not characteristic. There is no possibility of differentiating between glucurone and galacturonic acid.

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* I am indebted to Dr. LOUIS SATTLER, N.Y. Sugar Trade Laboratory, for a sample of ω-hydroxymethylfurfural.

RÉSUMÉ

Les aldo- et cétohexoses donnent avec le β-méthylindole un pigment soluble en bleu dans le chloroforme, de même que le ω-hydroxyméthylfurfural. Les pentoses et les acides uroniques donnent une coloration olive, comme le furfural, mais ils ne donnent pas de pigment soluble en bleu. Avec les méthylpentoses et le méthylfurfural, on a un pigment rouge; par extraction dans le chloroforme la coloration devient framboise. Le comportement des heptoses n'est pas caractéristiques. Il n'est pas possible de différencier le glucurone de l'acide galacturonique.

ZUSAMMENFASSUNG

Aldo- und Ketohexosen geben mit β-Methylindol ein Pigment, welches in Chloroform mit blauer Farbe löslich ist. Pentosen, Uronsäuren sowie Furfurol geben eine olivfarbige Reaktion, jedoch kein mit blauer Farbe in Chloroform lösliches Pigment. Methylpentosen und Methylfurfural geben ein rotes Pigment, das sich mit Himbeerfarbe in Chloroform löst. Das Verhalten der Heptosen ist nicht charakteristisch. Die Reaktion gibt keine Möglichkeit einer Unterscheidung von Glucuron- und Galakturonsäure.

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THE DETERMINATION OF SEMIMICRO QUANTITIES OF FORMIC ACID

by

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INTRODUCTION

For the determination of formic acid, most workers have used the method based on the ability of formic acid and its salts to reduce mercuric chloride to calomel according to the equation

$$NaCOOH + 2HgCl_2 = 2HgCl + HCl + NaCl + CO_2$$

The calomel produced has been determined both gravimetrically and volumetrically.

FRANZEN AND EGGER[1] described a mercuric chloride reagent for the determination which has usually been employed by subsequent investigators. The reagent contains sodium acetate and sodium chloride in addition to mercuric chloride. Acetate is present to take up the acidity produced which otherwise inhibits the reaction. Sodium chloride is included to allow more mercuric chloride to be dissolved but is known to decrease the reaction velocity when present in appreciable concentration[2].

Using this reagent, the method is suitable for the determination of formic acid in the presence of other volatile fatty acids. A disadvantage is that the method is somewhat time-consuming, the formate solution needing to be heated for at least two hours with the reagent. Moreover, it is unsuitable for quantities of formic acid less than 5 mg.

With the reagent described below, which contains no chloride and which is buffered at pH 5, the method can be extended to cover the determination of quantities as small as 0.1 mg. Furthermore, the time of heating is reduced to 30 minutes.

The method, which is a modification of the iodimetric method of RIESSER[3], is applicable to concentrations of formic acid, as sodium salt, of 0.1 — 2.5 mg/5 ml. The maximum error is less than two per cent.

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EXPERIMENTAL

Reagents

1. $0.166M$ mercuric chloride, 50 ml; $0.5M$ sodium acetate, 8 ml; $0.5M$ acetic acid, 3.5 ml; water to 100 ml. The acetate and acetic acid constitute a buffer at pH 5.
2. $2N$ hydrochloric acid.
3. potassium iodide solution, 10 g/100 ml.
4. Standard iodine solutions. These are of various concentrations from $0.005N$ - $0.025N$. The particular concentration which is used depends on the quantity of formate to be determined. They are conveniently prepared by dilution of a stock $0.1N$ solution.
5. $0.005N$ sodium thiosulphate solution. Prepared from a stock $0.1N$ solution.

Procedure

To 5 ml of formate solution in a 30 × 200 mm boiling tube are added 5 ml of the mercuric chloride reagent. The tube is covered with a glass bulb and placed upright, protected from the light, in a boiling water bath, for 30 min. After cooling the tube in water for 15 min the following reagents are added in order: 2 ml hydrochloric acid, 3 ml potassium iodide solution and 5 ml standard iodine solution. The tube is given a quick shake after the addition of potassium iodide to dissolve the mercuric iodide complex. It is then corked and shaken on a wrist action shaker at a speed sufficient to disperse the calomel. After 5 min the calomel is completely dissolved and the solution clear. The excess of iodine is back-titrated with $0.005N$ thiosulphate. A blank determination on 5 ml distilled water must be carried out at the same time.

The reaction between calomel and iodine in hydrochloric acid is $2\ HgCl + I_2 + 2HCl = 2\ HgCl_2 + 2\ HI$. Therefore each ml $0.005N$ iodine consumed by the the calomel is equivalent to 0.115 mg formic acid. Results of analyses are shown in Table I.

TABLE I

DETERMINATION OF FORMIC ACID

Formic acid taken mg	Normality of iodine added	ml $0.005N$ I_2 equivalent to formic acid calc.	Recovery %*	Standard Deviation
0.10	0.005	0.87	99.6	0.95
0.25	0.005	2.18	99.5	0.65
0.50	0.010	4.35	100.5	0.50
1.00	0.0125	8.70	99.1	0.10
1.50	0.020	13.05	99.4	0.26
2.50	0.025	21.75	98.7	0.37

*Mean of 6 determinations.

As the reaction between mercurous chloride and iodine is relatively slow, it is conveniently accelerated by vigorous mechanical shaking. An appreciable excess of iodine also helps to increase the rate of reaction. Iodine sufficient to give back-titration of at least 2.5 ml 0.005*N* thiosulphate should be added. The titration becomes unnecessarily time-consuming if large excesses are added.

ACKNOWLEDGEMENT

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SUMMARY

A method is described for the determination of small amounts of formic acid. Mercuric chloride, in acetate-buffered solution, is reduced to calomel by formate. The calomel produced is determined iodometrically.

RÉSUMÉ

Une méthode est décrite pour la détermination de petites quantités d'acide formique. Le chlorure mercurique, dissous dans un tampon à l'acétate, est réduit en chlorure mercureux par le formiate. On détermine le chlorure mercureux formé par l'iode et le thiosulfate de sodium.

ZUSAMMENFASSUNG

Eine Methode für die Bestimmung kleiner Mengen von Ameisensäure wird beschrieben. Quecksilberchlorid, in einem Azetatpuffer aufgelöst, wird durch Formiat zu Kalomel reduziert. Das Kalomel wird mit Jod und Natriumthiosulfat bestimmt.

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ÉTUDE SUR LE DOSAGE DE L'ÉTAIN DANS LES ALLIAGES LÉGERS À BASE D'ALUMINIUM

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OBJET DE L'ÉTUDE

La méthode étudiée dans un travail antérieur[1] et destinée au dosage de l'étain dans les alliages légers à base d'aluminium, a donné lieu, lors de sa mise en application en service courant, à quelques irrégularités qui seront mentionnées dans ce qui suit.

Une récente publication[2], ayant trait à l'utilisation de l'acide nitro-hydroxyphénylarsinique en vue du dosage néphélométrique de l'étain, a conduit à faire application de ce réactif dans le cas du dosage de cet élément dans les alliages légers; par là-même, se trouve éliminée la cause des anomalies rencontrées dans la méthode antérieurement décrite, en même temps que l'on bénéficie d'un gain en rapidité.

PARTIE EXPÉRIMENTALE

On rappelle que la technique donnée tout d'abord[1] consiste à séparer l'étain sous forme de sulfure; celui-ci est calciné, en creuset de porcelaine, puis en creuset de platine, et attaqué par fusion sodique; l'étain(IV) étant ensuite précipité sous forme de complexe silicotungstique d'hexaméthylènetétramine et d'étain, le dosage est terminé par le moyen de la mesure néphélométrique de la suspension, du complexe que donne l'étain avec le cupferron.

Il s'est produit qu'entre les mains de certains exécutants, des dosages ont été fortement erronés par défaut. Après examen des causes d'erreurs, il est apparu que c'est à la calcination du sulfure d'étain et peut-être aussi à la fusion qui lui fait suite, que doivent être rattachées ces anomalies. Celles-ci se produisent lorsque l'on fait usage de creusets de platine usagés et dépolis, mais non si ces instruments sont à l'état de neuf et bien polis; et l'on peut penser à un véritable étamage du platine, succédant à une réduction de l'étain, à la faveur du carbone du filtre calciné; cet écueil avait antérieurement amené à faire la calcination en creuset de porcelaine, puis la fusion sodique dans le platine. Les anomalies en question se produisent d'ailleurs, avec encore plus de netteté si la calcination et la fusion ont lieu en creuset de nickel. Après vérification des autres gestes

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opératoires (précipitation du sulfure d'étain, puis précipitation du complexe silicotungstique et néphélométrie au cupferron) en a pu conclure à leur parfaite validité; il est donc souhaitable bien que non absolument nécessaire que la calcination du sulfure et la fusion sodique soient évitées dans la méthode.

L'attention est attirée par KARSTEN, KIES ET WALRAVEN sur l'acide 3-nitro-4-hydroxyphénylarsinique comme réactif de dosage néphélométrique de l'étain; ce réactif est au reste connu, mais comme réactif du cadmium[3]. Les auteurs mentionnés l'appliquent au dosage de l'étain en présence d'antimoine, ces deux éléments ayant été séparés en commun sous forme de sulfures: ceux-ci sont dissous dans l'acide sulfurique, et la mesure néphélométrique avec l'aide du réactif suit immédiatement.

L'acide tartrique, que les auteurs ajoutent au milieu du dosage néphélométrique, est inutile dans le cas du dosage de l'étain dans les alliages légers, en raison de l'absence d'antimoine. L'on a pu constater que le repos prolongé après addition du réactif est inutile dans le cas actuel, et que la mesure peut intervenir après deux heures seulement de repos.

Le mémoire original mentionne de faire les mesures à 424 mμ, valeur que l'on a adoptée; que les éléments suivants: Ag, As, Bi, Cu, Cd, Mo, Zn, Ni, Co, Mo, Al, Cr, Fe, U, Ce, Mg, K, Pb et Hg sont sans effet nuisible; deux autres éléments, Ti et Zr, qui donneraient une réaction semblable à celle de l'étain, sont éliminés par les conditions mêmes de la précipitation initiale au sulfure.

En raison des caractéristiques de sensibilité de l'acide nitro-hydroxy-phénylarsinique vis-à-vis de l'étain, indiquées d'ailleurs par KARSTEN, KIES ET WALRAVEN, le maximum dosé d'étain est limité à 0.5 mg, soit une valeur quatre fois moindre que pour le cupferron (2 mg); pour une prise d'essai finale correspondant à 1 g d'alliage, on a dosé ainsi jusqu'à 0.05% Sn.

Grâce à l'attaque par l'acide sulfurique du sulfure, la calcination et la fusion sodique de celui-ci sont éliminées. Appliquer cette voie dans la méthode antérieurement décrite[1] serait peu pratique, en raison de la très grande quantité d'acide sulfurique mise en œuvre, de la neutralisation qui serait alors nécessaire en vue de la précipitation du silicotungstate d'hexaméthylènetétramine et d'étain, et de la grande dilution nécessaire pour tenir en solution tout le sulfate alcalin formé. L'on pourrait également songer à séparer initialement l'étain, non sous forme de sulfure, mais par distillation; mais là encore, l'acide chlorhydrique pur distillé nécessiterait la même neutralisation, et comporterait les mêmes écueils. C'est pourquoi la séparation du sulfure d'étain a été conservée.

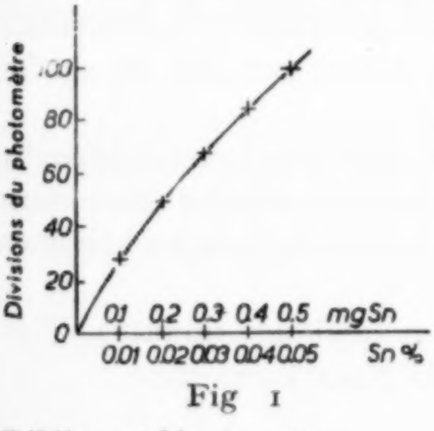

Fig 1

La méthode décrite en appendice permet le dosage de l'étain dans les métaux légers. La courbe (Fig. 1.) comporte les résultats obtenus dans l'établissement de la gamme d'étalonnage.

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APPENDICE

DOSAGE DE L'ÉTAIN DANS LES ALLIAGES LÉGERS

Principe: Après attaque du métal, précipitation de l'étain sous forme de sulfure, par le sulfure de sodium. Mise en solution sulfurique de l'étain.

Dosage néphélométrique par l'acide 3-nitro-4-hydroxyphénylarsinique.

Réactifs particuliers

1. Sulfure de sodium. Solution à 100 g/l.
2. Réactif à l'acide 3 nitro-4-hydroxyphénylarsinique. Dissoudre 1 g de réactif dans 15 ml d'alcool méthylique. Compléter à 50 ml avec de l'eau, filtrer si nécessaire. Ce réactif doit être fraîchement préparé.
3. Liqueur stannique type. Attaquer 1 g d'étain dans 25 ml d'acide chlorhydrique (1.18), diluer et oxyder par l'eau oxygénée. Porter à l'ébullition pour détruire l'oxydant, compléter au litre avec de l'eau. Diluer cette solution au dixième: 1 ml = 0.1 mg (à employer immédiatement après dilution).

Technique opératoire

1. Prise d'essai: 4 g.

Attaquer par 20 ml d'eau, et 45 ml d'acide chlorhydrique (1.18) que l'on ajoute par fractions de 10 ml pour modérer l'attaque. Si l'attaque est difficile, ajouter 0.15 g de chlorure de nickel cristallisé. Si l'alliage contient du cuivre, filtrer, laver à l'eau tiède. Oxyder par quelques gouttes d'acide chlorique (1.12), faire bouillir modérément afin de chasser le chlore. Refroidir.

2. Ajouter 100 ml d'eau, et 20 ml de solution de sulfure de sodium (à 100 g/l) (1). Chauffer à 70° environ. Laisser refroidir en agitant de temps en temps. Laisser le précipité se rassembler et déposer (4 à 5 heures, ou mieux une nuit). Filtrer (filtre bande bleue Durieux), laver à l'eau chlorhydrique (20 ml d'acide chlorhydrique (1.18) et 1 à 2 ml de sulfure de sodium (1) par litre), puis à l'eau.

3. Introduire le filtre et son contenu dans un erlenmeyer (250), ajouter 20 ml d'acide sulfurique (1.84), couvrir d'un petit entonnoir et chauffer modérément au début, et plus fortement sur flamme nue jusqu'à départ complet du soufre. Laisser refroidir.

Ajouter 2 g de persulfate d'ammonium et chauffer de nouveau. Laisser refroidir.

Le liquide doit être incolore. Sinon, ajouter encore 1 g de persulfate d'ammonium et chauffer de nouveau jusqu'à émission d'abondantes fumées sulfuriques blanches. Laisser refroidir.

4. Reprendre par 50 ml d'eau, porter à l'ébullition quelques minutes. Faire passer en fiole jaugée de 100 ml et compléter avec de l'eau à 100 ml.

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5. Prélever 25 ml de ce liquide, que l'on reçoit en fiole jaugée de 50 ml. Ajouter 10 ml d'eau, puis 10 ml de réactif (2). Compléter à 50 ml avec de l'eau. Agiter.

Laisser reposer 2 heures.

Gamme d'étalonnage

Faire 6 prises d'essais de 4 g d'aluminium exempt d'étain. Ajouter respectivement de la liqueur type d'étain (3) (1 ml = 0.1 mg):
0 4 8 12 16 20 ml
contenant respectivement
0 0.4 0.8 1.2 1.6 2 mg Sn
soit en % de la prise d'essai:
0 0.1 0.002 0.003 0.004 0.005% Sn
Suivre le mode opératoire.

Mesures photométriques

Méthode du témoin unique (terme O de la gamme)
Cuves de 2; $\lambda = 425$ mμ
Précision: ± 3% en valeur relative.

RÉSUMÉ

Une technique de dosage de l'étain dans les métaux légers à base d'aluminium est indiquée: il est fait usage de l'acide nitrohydroxyphénylarsinique comme réactif néphélométrique de l'étain.

SUMMARY

A method of determining tin in light aluminium alloys is described; nitrohydroxyphenylarsinic acid is used as nephelometric reagent for tin.

ZUSAMMENFASSUNG

Es wird eine Bestimmungsmethode von Zinn in Leichtmetallen auf Aluminiumgrundlage gezeigt. Es wird dabei von Nitrohydroxyphenylarsinsäure als nephelometrisches Reagenz für Zinn Gebrauch gemacht.

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DETERMINATION OF OXYGEN IN TIN METAL BY THE AMALGAM METHOD *

by

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The determination of combined oxygen in a metal which is to be viewed as a corrosive liquid because of its low melting point and its miscibility with certain other metals is of interest for various reasons. In the case of tin, unsuspected corrosive properties may be contingent upon, and be caused by, the oxygen content.

Vacuum fusion techniques for determining oxygen are frequently used for steels and for titanium metal[7]; but for bismuth metal[1] and for copper metal, hydrogen reduction of the copper oxide is simpler[5]. A newer idea, applied to sodium metal, is the use of mercury. PEPKOWITZ AND JUDD[3] used mercury as solvent for sodium metal, leaving sodium oxide as an insoluble residue. The sodium oxide is then dissolved in water and titrated with standard acid, and oxygen is determined by calculation. Based on the mercury-solvent plan, this paper outlines a method for the determination of oxygen in tin, and the technique is adapted to the specific properties of mercury, tin metal and tin oxide. In this work, it is assumed that all of the oxygen is present as SnO (stannous oxide).

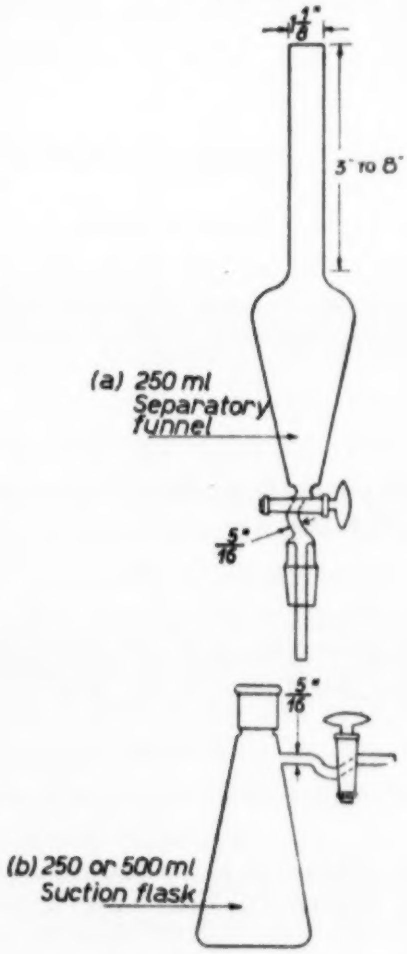

Fig. 1

If tin metal and mercury are shaken in air, a dark powder soon covers the surface of the mercury. It is therefore necessary to prepare and treat the tin amalgam in absence of air. Accordingly, a convenient apparatus (Fig. 1) was designed, wherewith the tin may be separated from the tin oxide as soluble tin amalgam in vacuum. In this procedure, mercury metal is the "washing liquid", and "washings" are performed until the "wash mercury" contains no tin metal, by test.

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* This report is based on studies conducted for the Atomic Energy Commission under Contact AT-11-1-Gen-8.

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As soon as the tin metal has been removed, the tin oxide in the flask is dissolved with aqueous hydrochloric acid and hydrogen peroxide, and the tin content of this solution is determined by the blue phosphomolybdate method[4,6]. The colorimetric determination of tin by the molybdenum blue method was simplified in the present investigation to a rapid, reproducible routine, and this method was chosen because of its inherent superiority over the silico-molybdate method[4], and the toluene-3,4-dithiol method[4].

SOLUTIONS AND REAGENTS

Ammonium hydroxide, c.p., sp.g. 0.9
n-*Amyl alcohol*, reagent grade
a, a'-dipyridyl, 0.2 mg per 100 ml of water
Ferric chloride solution, 0.5 g $FeCl_3 \cdot 6\ H_2O$ and 5 ml of hydrochloric acid (sp. g. 1.2) in 95 ml of water
Hydrochloric acid, c.p., sp.g. 1.2
Hydrochloric acid solutions, 1 : 2 and 1 : 10 with water
Hydrogen peroxide, 3 per cent.
Mercury, reagent grade, (tested for dissolved tin or reducing agents)
Molybdic acid, or sodium molybdate, c.p.
Phosphomolybdate reagent

Solution A. Dissolve 2.5 g of molybdic acid in 50 ml of 4 per cent. (aqueous) sodium hydroxide solution. Cool below room temperature. Prepare a cold 6 per cent. (3 ml of acid per 50 ml of water) sulfuric acid solution, and slowly, with stirring, add the acid solution to the alkaline solution. This will keep for about 6 months.

Solution B. Dissolve 0.44 g of sodium dihydrogen phosphate in 100 ml of water.

Solution C.M ix 10 ml of Solution A and 4 ml of Solution B, then dilute to 200 ml with water. Mix well. Discard after 8 hours.

Sodium bicarbonate, 8 per cent. in water
Sodium di-hydrogen phosphate, c.p.
Sodium hydroxide solution, 4 per cent. in water
Sulfuric acid, c.p., sp.g. 1.84
Tin metal
Zinc, c.p., 20 mesh or larger sizes

PROCEDURE

The apparatus in Fig. 1 is all of pyrex. The part marked A consists of a 250-ml pyrex pear-shaped separatory funnel to the mouth of which a pyrex glass tube 3″ to 8″ in length and about 1-1/8″ in diameter has been fused, and to the other end of the funnel a ground glass connection has been fused along with an insert tube. Part B is a suction flask carrying a ground glass one-way stopcock. The glass tube (3″ to 8″) is of such length that several tests may be performed before discarding or reconstructing the apparatus.

Operation of the tin amalgam apparatus

Insert the weighed sample (1 to 5 mg) of tin through the open tube, then seal the glass. Place clean mercury (about 200 times the weight of the tin) in the suction flask, attach the flask to the separatory funnel, open the stopcocks and evacuate the apparatus. Close the stopcock on the suction flask, invert the complete apparatus as a unit and allow about one-half of the mercury to drain into the funnel, then close this (funnel) stopcock. Turn the apparatus to the upright position, open the suction flask stopcock to air (funnel stopcock closed) then detach the suction flask.

To hasten the solution of the tin in mercury, invert the funnel and set the long tongue in a bath of boiling water. Occasionally remove the funnel from the water bath and shake the liquid to aid the solution process. This takes 30 to 60 minutes.

When solution is complete, allow the apparatus to cool; then set it in the upright position. Attach a "dirty" suction flask "C" to the funnel, evacuate the flask, then drain about nine-tenths of the amalgam into the empty, "dirty" flask. With the funnel stopcock closed, open the suction flask stopcock to air, then detach the "dirty" flask and discard the liquid. Re-attach the "clean" flask "B", containing clean mercury, evacuate the flask and invert the funnel so that the mercury covers the outlet tube of the separatory funnel. Drain about 10 ml of clean mercury into the funnel, close the funnel stopcock, set the funnel in its upright position, open it to air, and remove the suction flask "B". Slosh the mercury around the funnel, as in a "washing" operation, then set the funnel in its upright position. Attach the "dirty" flask C, evacuate the flask, drain about nine-tenths of the mercury into the "dirty" flask C, close the funnel stopcock and open the flask stopcock to air.

Re-attach the "clean" flask B, and repeat the mercury washing cycle five times, except that for the sixth drainage, a new flask D, is used to catch the wash mercury. This portion of wash mercury is used to test for "Completeness of Washing", as described below. If tin is still present in the mercury, perform 2 more washings and test again. When the wash mercury is free of tin, proceed to the next step.

Test for completeness of washing

Run the tin-amalgam wash into a small separatory funnel containing 10 ml of (1:2) hydrochloric acid solution. Mix, in order to extract tin from the mercury layer into the acid layer. Drain out the lower (mercury) layer and retain the water layer. To the water layer in the funnel add 2 ml of 0.5 per cent. ferric chloride solution and 1 ml of dipyridyl indicator solution. Drop in a piece of Congo Red paper and add (1 : 1) ammonium hydroxide until the paper just turns red. Add about 0.1 gram of ammonium bifluoride, mix and add (1:10) hydrochloric acid solution until the paper just turns blue again. A red color solution indicates the presence of tin.

Preparation of test and standard solutions

After the wash mercury has been found free of tin, add about 100 ml of (1:2) hydrochloric acid solution to flask D, attach it to the funnel, invert the apparatus, suck about 15 ml of the aqueous solution into the funnel, close the funnel stopcock and set the apparatus in its upright position. Drain all the mercury into the suction flask, then close the stopcock. Remove the flask, pour the contents into a separatory funnel, separate, reserve the acid solution, and discard the mercury. Attach a new suction flask "E" to the apparatus and drain the hydrochloric acid solution from the funnel into the flask E. Using the above technique, for a second time suck 15 ml of the hydrochloric acid solution into the funnel, wash and drain into flask E; and for the third time suck in 10 ml of the hydrochloric acid solution plus 1 ml of 3 per cent. peroxide, wash and drain into flask E. The separatory funnel should now be clean and the test solutions are combined in flask E.

Transfer the test solution to a 125-ml Erlenmeyer flask. Also prepare a series of 4 similar flasks, and add to the respective flasks standard solutions containing 0.00 mg, 0.10 mg, 0.30 mg and 0.50 mg of tin. Dilute these solutions to 50 ml with (1:2) hydrochloric acid solution.

To each flask add about 1 gram of zinc (20 mesh or larger) and heat to displace air in the flask. When the air in the flask is quite cloudy, insert a one-hole rubber stopper containing a capillary tube into the neck of each flask and continue heating for two or three minutes.

Prepare a group of five 125-ml separatory funnels and add 15 ml of Solution C (phosphomolybdic acid) to each. Place a small funnel, containing a wad of glass wool, in the neck of the separatory funnel. After a flask has been heated for a sufficient period of time, cool the flask under running water, remove the stopper and decant the tin solution through the glass wool into the separatory funnel. Wash once by decantation with (1:2) hydrochloric acid solution. Remove the small funnel, add 1 to 2 ml of 8 per cent. sodium bicarbonate solution, mix and stopper the flask. Allow the blue solution to develop for 5 to 10 minutes.

Remove the stopper from the separatory funnel, add 20 ml of *n*-amyl alcohol and shake to extract the blue solution. Allow the two layers to separate and drain out and discard the lower (aqueous) layer. Run the blue alcoholic solution into a 25-ml volumetric flask, dilute to the mark with *n*-amyl alcohol and mix well.

RESULTS AND DISCUSSION

Colorimetric determination of tin

The phosphomolybdate method for tin was unfavorably reported by SANDELL[4]; but, in the procedure described in this report, the apparent difficulties have been overcome. A low, consistent blank has been obtained and reproducible results are to be expected. The working range of tin weights corresponding to different extract volumes of amyl alcohol are summarized in Table III. The reading for 0.7 mg of tin in 25 ml of amyl alcohol, listed in Table II, is as high as 700 (see Note e, Table II) on the photometer scale, which is considered to be quite high for a working range in the blue. Above this concentration, the curve will tend to deviate from Beer's Law.

Data for the preparation of photometer calibration graphs are presented in Table II. The photometer readings shown have been corrected for the "0.0 mg" tin reading. (This photometer reading was about 100). For any one preparation of the phosphomolybdate reagent, the graph of tin weights vs. photometer readings (corrected for blanks) is a straight line. However, the slope of the line may change from one batch of reagent to another; and may change with the age of the preparation within a single batch. It is for this reason that three tin standards are included in each test run.

TABLE I

DETERMINATION OF OXYGEN IN TIN

Run No.	Type of sample	Weight of sample	Weight of tin in dross from amalgam (mg)	Oxygen (mg) (a)	Oxygen %
1.	Block Tin (b)	2.2345	0.015	0.0020	0.00009
2.	Block Tin	3.6003	0.007	0.0009	0.00003
3.	c.p. Tin (d)	5.1160	0.10	0.014	0.0003
4.	c.p. Tin	4.9620	0.06	0.0081	0.0002
5.	Filtered Tin (c)	5.7862	0.22	0.030	0.0005
6.	Filtered Tin	11.147	0.05	0.0067	0.00006

(a) These weights of oxygen are computed from the weights of SnO, equivalent to the tin values in the previous column.
(b) Commercial block tin was obtained locally.
(c) Filtered tin was prepared by melting granulated c.p. tin in vacuum, followed by filtration through a fine porosity sintered pyrex filter.
(d) c.p. tin, granulated ("Baker's Analyzed").

TABLE II

KLETT-SUMMERSON PHOTOMETER CALIBRATION DATA

Weight of tin taken (mg)	Weight of equivalent oxygen (mg)	Photometer readings					
0.0	0.0						
0.05					68(c)		
0.1	0.014	54(a)	61(b)	99(c)		122(d)	
0.2	0.027	118					
0.25					266	204	188(e)
0.3	0.040	165	161	301			
0.35					360		
0.4	0.054						
0.45					450		253
0.5	0.068	258	264	504		512	
0.55							289
0.6	0.081						405
0.7	0.094	316	416				

(a) and (b) are same batch of Solution C (see Appendix A), but (b) was made up 2 hours later; (c) (d) and (e), other batches, for duplication tests.

TABLE III

Volume of amyl alcohol (ml)	Range of tin weights
10	2 . . . . 200 micrograms
25	0.02 . . . . . 0.70 mg
50	0.7 . . . . . . 1.2 mg

Table I summarizes the results obtained with the amalgam method. The weights of tin listed in the fourth column of the table were read from photometer calibration graphs (prepared from observations on standard solutions of tin).

The relatively higher oxygen content observed for c.p. tin than for commercial block tin may arise from the higher surface-to-weight ratio of the c.p. tin granules.

Insolubility of stannous oxide in mercury

The dark powder which forms on the surface of tin amalgam when it is shaken in air was shown to be stannous oxide, SnO, by the mercuric chloride test and the ferric chloride-phenanthroline reaction.

Samples of the SnO powder, prepared as indicated above, were shaken with clean mercury and the mercury layer then tested for tin content according to the procedure of Appendix B. No tin was detected, indicating that SnO is insoluble in mercury.

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Reducing agents for tin solutions

The choice of reductant for tin was limited to zinc and aluminum metal. Zinc, (c.p. grade) gave a lower blank, and was therefore selected for use. The sample of aluminum used (type 2S) may have contained undesirable impurities; it is possible that c.p. aluminum may be more satisfactory.

Color stability

Tests were made to investigate the effect of hydrochloric acid concentration on the stability of the blue phosphomolybdate color. Concentrations less than 1:3 or greater than 1:1 yielded inconsistent results. The 1:2 concentration was therefore selected and used.

In the poorest cases, using 1:2 hydrochloric acid, the blue color was found to be stable for about 45 minutes, to decrease slightly in intensity over the next 15 minutes, and then to deteriorate rapidly.

The amyl alcohol extract was always clear.

Interfering elements

The only foreign element to cause difficulty with the amalgam separation method is sulfur, which would yield high results because of the very probable insolubility of tin sulfide in mercury. Sulfur was not found to be present in the (c.p.) grades of tin used in this investigation.

Foreign metals which may be present in the tin (antimony, arsenic, bismuth, cadmium, copper, iron, lead or zinc) are washed away by the mercury, or removed by the zinc reduction, or do not inherently interfere[6].

Photometric determination

Use water to set the instrument at 100 per cent. transmittancy, using a 660 μ filter. Obtain the transmittancies of the standards and test samples, on the logarithmic scale, and subtract the "0.0 mg Sn" reading from the apparent readings for the standards and unknowns. Plot corrected "transmittancies" as ordinate and "mg Sn" as abscissa. For the test samples, the corrected "transmittancy" value is used to obtain the corresponding "mg Sn" from the calibration curve.

Calculation:

$$\text{Per cent. oxygen} = \frac{\text{Weight of Sn (mg)} \times 0.135 \times 100}{1000 \times \text{Weight of tin sample}}$$

ACKNOWLEDGEMENTS

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SUMMARY

In vacuum, tin metal is completely separated from stannous oxide by mercury. The tin content of the stannous oxide is then determined colorimetrically by an improved blue phosphomolybdate solution technique; and from the tin result, the oxygen is calculated. The procedure is satisfactory for the determination of oxygen concentrations of 0.0001% or less in tin metal samples weighing 2-5 mg.

The apparatus developed for the vacuum preparation and treatment of the amalgam is described.

RÉSUMÉ

Dans le vide, l'étain métallique est séparé quantitativement de l'oxyde d'étain(II) par le mercure. La teneur en étain est alors déterminée colorimétriquement par la réaction bleue du phosphomolybdate. On calcule ensuite la teneur en oxygène à partir de la quantité d'étain trouvée. Ce procédé permet de doser des concentrations de 0.0001%, ou moins, d'oxygène dans des échantillons d'étain de 2 à 5 mg. On décrit l'appareil utilisé pour la réaction dans le vide et le traitement de l'amalgame.

ZUSAMMENFASSUNG

Im Vakuum wird metallisches Zinn vom Zinn-II-Oxyd mit Quecksilber vollständig abgetrennt. Der Zinngehalt des Zinn-II-Oxyds wird dann colorimetrisch durch eine verbesserte Methode mit blauer Phosphomolybdatlösung bestimmt und aus dem Zinngehalt wird der Sauerstoff berechnet. Das Verfahren ist befriedigend zur Bestimmung von Sauerstoff in Konzentrationen von 0.0001% oder weniger n Zinnmetallproben von 2-5 mg Gewicht.

Der zur Vakuumdarstellung und Behandlung des Amalgams entwickelte Apparat wurde beschrieben.

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SÉPARATION CHROMATOGRAPHIQUE VANADIUM/MOLYBDÈNE, SUR PAPIER A L'ÉCHELLE DU MICROGRAMME, MISE AU POINT DES TITRAGES DIRECTS

par

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Le vanadium et le molybdène, voisins dans la classification périodique, ont des propriétés très semblables et réagissent identiquement avec de nombreux réactifs. On les trouve souvent réunis soit comme oligo-éléments dans le sol et les êtres vivants, comme impuretés dans les minerais, soit incorporés dans des alliages, mais presque toujours à l'état de traces. Le molybdène intervient dans les aciers spéciaux dans des proportions qui peuvent varier de 0.1 à 7% (parfois même jusqu'à 19%), le vanadium s'y trouve en quantité inférieure à 0.05%.

L'importance du dosage de ces éléments est accrue du fait de leur action biochimique à l'état de traces. Ils interviennent dans le métabolisme des cellules végétales et animales.

La séparation vanadium/molybdène par voie chimique est difficile à cause des interférences mutuelles; elle est pourtant nécessaire pour procéder au dosage de ces éléments lorsqu'ils existent en mélange.

La méthode chromatographique sépare ces éléments sur papier, automatiquement et quantitativement à l'échelle du microgramme, en un temps compris entre 180 et 240 minutes au maximum.

Ce n'est pas une analyse sur goutte (Tüpfelanalyse) qui est proposée ici, mais bien une séparation quantitative de tache de ces éléments mélangés, déposés sur papier, de façon à pouvoir ultérieurement découper ces taches individuellement et les doser.

La détermination du vanadium et du molybdène ainsi séparés a également fait l'objet de ce travail. Alors qu'il est d'usage de se baser sur la révélation qualitative des taches pour juger de la séparation chromatographique (choix du saturant et du développant) nous avons complété ce critère par un *titrage direct des éléments* à même le papier. L'élution que nous avons pratiquée jusqu'ici en vue du contrôle quantitatif a été supprimée dans le présent travail et avec elle, les interférences possibles de l'élément et des éléments du papier entraînés.

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Cette titration directe du molybdène et du vanadium chromatographiés se révèle particulièrement intéressante pour „prospecter" directement chaque portion de bandelette chromatographiée. Cette nouvelle technique d'investigation nous a fourni des renseignements importants sur la migration de certains ions complexants et sur le comportement du papier vis-à-vis du vanadium chromatographié, à cause de la facile réductibilité et oxydabilité du vanadium.

Des horizons nouveaux s'ouvrent ainsi pour éclaircir la connaissance de phénomènes intimes se passant dans le papier au cours d'une chromatographie.

Le titrage direct du molybdène, mis au point au cours d'un autre travail[1] a servi ici pour corroborer les résultats quantitatifs obtenus pour le vanadium dans les séparations vanadium-molybdène.

PARTIE QUALITATIVE

1. *But de la séparation*

Le but poursuivi dans ce chapitre est l'obtention à partir d'une solution de molybdène et de vanadium mélangés, de taches tout à fait *nettes* et *séparées* de vanadium et de molybdène pour pouvoir par la suite les découper et les doser sans interférence.

La méthode employée diffère de celle des laboratoires étrangers.

POLLARD et autres[2] combinent la chromatographie sur papier avec l'analyse sur goutte. Ils séparent un certain nombre d'éléments groupés en une tache et révèlent successivement les constituants d'une même tache à l'aide de réactifs analytiques organiques spécifiques. Ex.: l'argent, le cuivre et le nickel ont des taches superposées mais révélées différemment: au chromate de potassium pour l'argent, à la dithioxamide pour le cuivre et le nickel. Leur but n'est pas d'obtenir des taches séparées, mais la possibilité *d'identifier tous les éléments* dans une tache complexe.

Ce procédé ne conduit qu'exceptionnellement à une possibilité de dosage et ce, lorsque les différents éléments formant la tache chromatographiée n'interfèrent pas dans la détermination l'un de l'autre. Les conditions chromatographiques qui séparent nettement les éléments les uns des autres donnent les meilleures conditions pour le dosage ultérieur, en laissant plus de liberté pour le choix de la détermination. Un tel résultat n'est possible qu'en étudiant à fond les solvants propres à développer chacun des éléments en taches séparées. Cette étude est laborieuse et empirique: seule la liste de STRAIN[3] constitue un guide et plusieurs centaines de solvants (environ 250 dans ce cas ci) sont souvent passés en revue avant de trouver les conditions chromatographiques optima.

Une autre différence avec les laboratoires étrangers est que nous évitons d'employer des développants complexants ou contenant des substances complexantes susceptibles de perturber la possibilité de dosages ultérieurs. Ainsi, dans ce travail,

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il a été démontré que l'ion tartrique dans la solution d'éléments est un obstacle au titrage direct du molybdène et du vanadium.

L'emploi de réactifs complexants met les autres chercheurs dans l'obligation d'incinérer le papier portant l'élément, avant de procéder à son dosage. Ceci n'est pas sans danger pour les éléments comme le chrome, susceptible d'être volatilisé à température plus ou moins élevée. L'absence de complexe dans les solutions et dans les solvants nous a permis, à Bruxelles, jusqu'ici, de doser les éléments directement dans l'éluat.

La durée des séparations effectuées ici est de 30 à 240 minutes selon le mode de développement employé, tandis qu'à l'étranger, elles nécessitent de 8 à 12 et même 24 heures.

2. *Technique employée*

La description détaillée du procédé habituel employé a été donnée dans des mémoires précédents[4]:

Rappelons que la chromatographie se fait dans une cuve en verre (38 cm × 28 × 25) saturée pendant 12 heures par le saturant désiré.

Les bandelettes en papier Whatman No. 4 ont 1 cm de large et 25 cm de long. Les prises du mélange des cations à séparer sont faites à l'aide d'une microburette horizontale[5] de 0.1 ml $\pm$ 0.0002 ml (soit 10 μg de chaque élément) et déposées à 3.5 cm du bord supérieur. Les extrémités supérieures des bandelettes sont placées dans le développant; le développement est descendant.

Nous utilisons dans ces essais un développant différent du saturant selon la méthode employée avec succès lors de la séparation silicate-borate-molybdate, aluminium-uranium-fer et cuivre-nickel-cobalt[6].

Le vanadium et le molybdène sont révélés tous deux par vaporisation à l'oxine acétique sur les bandelettes de papier chauffées à 35-38° C: 1 gramme d'hydroxyquinoléine dissous dans 24 g d'acide acétique glacial additionné de 16 g d'eau bidistillée; cette solution stock est diluée trois fois. A 100 ml de cette dernière, on incorpore 10 g d'acétate de sodium.

3. *Résultats qualitatifs des chromatogrammes vanadium-molybdène*

(relatifs à des prises de 10 μg de chaque élément).

Pour s'orienter et faciliter l'interprétation des chromatogrammes, les solutions expérimentées au début ne renferment qu'un seul élément; les différences pouvant résulter du fait du mélange sont minimes. L'aspect des taches peut faire prévoir une séparation, mais leur forme n'est pas toujours celle désirée: il peut y avoir dispersion ou trop peu d'espace entre 2 taches voisines. Ultérieurement, le dosage a montré que des taches apparemment séparées peuvent contenir des quantités de l'autre élément, non révélables sur papier (voir quantitative).

Les développements ascendants et descendants ont été essayés, mais le déve-

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loppement descendant adopté est plus efficace, plus rapide et donne des taches plus nettes comme le prouve le tableau I.

Dans ce tableau, A représente la distance du dépôt à la tête de la tache, B la distance du dépôt à la fin de la tache, C la distance du dépôt au front liquide. Les rapports $\frac{A}{C}$ et $\frac{B}{C}$ restent constants pour un développant donné[7]. Par rapport aux valeurs R_F mentionnées dans la littérature, $\frac{A}{C}$ vaut R_{F_q} et $\frac{B}{C}$ vaut R_F (voir Tableau I).

TABLEAU I

Qualité du développement	Elément	Traitement de la prise	Durée	Rapport $\frac{A}{C}$ — $\frac{B}{C}$
Développement descendant	V^{+5}	p.s.	250′	0.25—0.45
		p.n.s.	250′	0.17—0.37
Développement ascendant	V^{+5}	p.s.	315′	0.15—0.55
		p.n.s.	315′	0.35—0.60
Développement descendant	Mo^{+6}	p.s.	250′	0.75—1.00
Développement ascendant	Mo^{+6}	p.s.	315′	0.67—1.00

Les expériences sur prises séchées (p.s.) se font sur bandelettes qui ont été laissées 10 minutes à 35° C., sous une lampe à rayons infra-rouges avant le développement. Les expériences sur prises non séchées (p.n.s.) sont faites sur bandelettes ayant été placées directement dans le développant, sans subir aucun traitement préalable.

Plusieurs types de solutions de molybdène et de vanadium ont été expérimentées (voir plus loin).

Le ***saturant*** contenait 50 ml de chloroforme et 50 ml de méthyléthylcétone; le ***développant***, 71 ml d'acétone, 20 ml de chloroforme et 9 ml d'acide chlorhydrique concentré.

Nous donnons ici un extrait des expériences qualitatives conduisant au développement convenant le mieux à la séparation des taches. Les rapports $\frac{A}{C}$ et $\frac{B}{C}$ n'ont pas été donnés quand la séparation obtenue n'était pas suffisante ou lorsque l'expérience n'a été faite qu'une ou deux fois.

Composition des solutions d'éléments

Ces solutions, qui contiennent toutes 10 μg de chaque élément au 0.01 ml, sont constituées comme suit: (nous donnerons chaque fois le symbole employé dans les tableaux suivants).

1. La solution „neutre" contient les vanadate ou(et)molybdate d'ammonium dissous dans l'eau bidistillée, (n).
2. La solution alcaline contient en plus du 1°, 7.5 g d'hydroxyde de sodium dans 100 ml, (a).
3. La solution tartrique contient 7.5 g d'hydroxyde de sodium et 10 g d'acide tartrique dans 100 ml, (t).
4. La solution acétique-sodique-acétate de sodium contient: 12 g d'acide acétique glacial, 16 g d'acétate de sodium et 7.5 g de d'hydroxyde de sodium dans 100 ml, (HAc-Na-AcNa).
5. La solution acétique-chlorhydrique contient 12 g d'acide acétique glacial et 10 ml d'acide chlorhydrique concentré dans 100 ml, (HAc-HCl).
6. La solution chlorhydrique contient 10 ml d'acide chlorhydrique concentré dans 100 ml, (HCl). Une solution contenant 30 g de HCl % p./v. a aussi été utilisée.

TABLEAU II

RÉSULTATS QUALITATIFS DES DEVELOPEMENTS DESCENDANTS

Exp.	Saturant	ml	Dévelop-pant	ml	Prise		Nature de la Prise				Observations
					p.s.	p.n.s.	[a]	[HCl]	[HAc-Na AcNa]	[HAc -HCl]	
1	M.E.C. $CHCl_3$	50 50	Acétone $CHCl_3$ HCl conc.	71 20 9	+	+	+				Séparation
2	M.E.C. $CHCl_3$	45 55	Acétone $CHCl_3$ HCl conc.	71 20 9	+	+	+				idem
3	M.E.C. $CHCl_3$	55 45	Acétone $CHCl_3$ HCl conc.	71 20 9	+	+	+				idem
4	M.E.C. $CHCl_3$	50 50	Acétone $CHCl_3$ HCl conc.	71 20 9	+	+		+			V dispersé Mo au F.L.

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Exp.	Saturant	ml	Dévelop-pant	ml	Prise p.s.	Prise p.n.s.	Nature de la Prise [a]]HCl]	Nature de la Prise [HAc-Na AcNa-]	Nature de la Prise [HAc- -HCl]	Observations
5	M.E.C. CHCl$_3$	id.	id.	id.	+	+		+		V dispersé Mo au F.L.
6	id.	id.	id.	id.	+	+			+	V dispersé Mo au F.L.
7	Acétone CHCl$_3$	50 50	id.	id.	+	+		+		V et Mo dispersés
8	CHCl$_3$ M.E.C. Acétone	40 40 20	id.	id.	+	+				V et Mo dispersés
9	CHCl$_3$ M.E.C.	75 25	id.	id.	+	+		+		V déplacé et + ramassé Mo grandes taches au F.L.
10	Benzène	100	Acétone CHCl$_3$ HCl conc.	71 20 9	+	+	+			Belles taches
11	Alc.amyl.	100	Acétone CHCl$_3$ HCl conc.	71 20 9	+	+		+		bonne séparation: V *A/C* 0.16 *B/C* 0.57 Mo *A/C* 0.72 *B/C* 1.00
12	Alc.amyl.	100	Acétone Alc.amyl. CHCl$_3$ HCl conc.	66 5 20 9	+	+		+		mauvaise séparation
13	Alc.amyl. Benzène	60 10	Alc.amyl. Benzène HCl conc.	60 10 30	+	+		+		séparation, mais **pas** quantitative
14	M.E.C. CHCl$_3$	50 50	Acétone Alc.amyl. CHCl$_3$ HCl conc.	61 5 25 9	+			+		V et Mo dispersés
15	M.E.C.	100 100	Alc.amyl. CHCl$_3$ HCl conc.	64 20 16	+			+		V et Mo déplacés au même niveau

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Exp.	Saturant	ml	Développant	ml	Prise p.s.	Prise p.n.s.	Nature de la Prise $\left[\frac{HAc\text{-}Na}{AcNa}\right]$	Nature de la Prise [HCl]	Observations
16	Alc.amyl.	100	Acétone $CHCl_3$ HCl conc.	71 20 9	+	+	+		bonne séparation: V *A/C* 0.19/0.20 *B/C* 0.61/0.63 Mo *A/C* 0.61/0.69 *B/C* 1.00/1.00
17	Alc.amyl. $CHCl_3$	60 10	Acétone $CHCl_3$ HCl conc.	71 20 9	+		+		V *A/C* 0.24 *B/C* 0.65 Mo *A/C* 0.79 *B/C* 1.00
18	Alc.amyl.	100	Acétone $CHCl_3$ HCl conc.	71 20 9	+		+		V *A/C* 0.25/0.25 *B/C* 0.64/0.65 Mo *A/C* 0.75/0.75 *B/C* 1.00/1.00
19	Alc.amyl.	100	Acétone $CHCl_3$ HCl conc.	71 20 9	+	+		+	V *A/C* 0.22/0.20 *B/C* 0.55/0.55 Mo *A/C* 0.70/0.70 *B/C* 1.00/1.00

Exp.	Saturant	ml	Développant	ml	Durée	Prise	Nature de la Prise	Observations
20	Alc.amyl. Benzène HCl conc.	60 10 30	S = D		240′	p.s.	HCl	*A/C* *B/C* V 0.06-0.36 0.08-0.38 0.07-0.37 0.01-0.39 Mo 0.68-1.00 0.70-1.00 0.71-1.00 0.75-1.00
21	Alc.amyl. Benzène HCl conc.	60 10 30	Alc.amyl. HCOOH	50 50	75′	p.s.	neutre	séparations: V/Mo W/Mo W, V, Cr au dépôt
22	Alc.amyl. Benzène HCl conc.	60 10 30	Alc.amyl. HCOOH	25 75	240′	p.s.	neutre	W/Cr V, Mo dispersés
23	Alc.amyl. Benzène HCl conc.	60 10 30	Alc.amyl. HCOOH	60 40	85′	p.s.	neutre	W/Mo Cr/Mo V/Mo W, V, Cr au dépôt
24	Alc.amyl. Benzène HCl conc.	60 10 30	Alc.amyl. HCOOH	40 60	120′	p.s.	neutre	W/Mo W/Cr W/V W au dépôt

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Exp.	Saturant	ml	Dévelop-pant	ml	Durée	Prise	Nature de la Prise	Observations
25	Alc.amyl. Benzène HCl conc.	60 10 30	Alc.amyl. HCOOH	45 55	90′	p.s.	neutre	W/Mo (W/Cr, W/V ébauchées, belles taches)
26	Alc.amyl. Benzène HCl conc.	60 10 30	Alc.amyl. HCOOH	45 55	180′	p.s.	neutre	*A/C* *B/C* W-0.00/0.06-0.10 V-0.16/0.12-0.37/0.31 Cr-0.16/0.17-0.43/0.38 Mo-0.39/0.32-0.66/0.56
27	Alc.amyl. Benzène HCl conc.	60 10 30	Alc.amyl. HCOOH	45 55	240′	p.s.	neutre	W-0.00/0.00-0.06 V-0.15/0.24-0.37/0.43 Cr-0.21/0.20-0.44/0.43 Mo-0.44/0.49-0.68/0.77
28	Alc.amyl. Benzène HCl conc.	60 10 30	Alc.amyl. HCOOH	45 55	180′	p.s.	HCl	W-0.00/0.00-0.05 V-0.10 -0.34 0.11 -0.35 0.12 -0.36 Mo-0.40 -0.56 0.41 -0.57 0.44 -0.59 0.44 -0.60
29	Alc.amyl. Benzène HCl conc.	60 10 30	Alc.amyl. HCOOH	45 55	240′	p.s.	HCl	W-0.00 -0.06 V-0.11/0.15-0.38/0.35 Cr-0.15/16/15/16-0.38/38/39 Mo-0.59/56/58-0.71/71/70
30	Acl.amyl. Benzène HCl conc. 5ème jour de saturation	60 10 30	Alc.amyl. HCOOH	45 55	240′	p.s.	HCl 30% v/v	W-0.00 -0.05/06 V-0.19/15/14-0.41/40/39 Cr-0.18/17/16-0.38/35/38 Mo-0.55/48/49-0.65/61/66
31	Alc.amyl. Benzène	60 40	Alc.amyl. HCOOH	25 75	95′	p.s.	neutre	W/Mo W/Cr mauvaises taches Mo
32	Benzène		Alc.amyl. HCOOH	25 75	95′	p.s.	neutre	W/Cr Mo, W au dépôt
33	Alc.amyl. Benzène	60 40	Alc.amyl. HCOOH	45 55	50′	p.s.	neutre	W/Cr
34	Alc.amyl. HCOOH	50 50	Alc.amyl. Benzène HCl conc.	60 10 30	160′	p.s.	neutre	W/Mo belles taches de V, Cr
35	Alc.amyl. Benzène HCl conc.	60 10 30	Alc.butyl. HCOOH	45 55	95′	p.s.	neutre	W au dépôt, séparations W/Mo, W/Cr, W/V

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Le tableau suivant montre l'influence de la mise en solution sur les résultats de la séparation.

TABLEAU III

					Prise		Nature de la Prise			
Exp.	Saturant	ml	Développant	ml	p.s.	p.n.s.	[n][a]	[HAc-Na -AcNa]	[HCl p/v 30g%]	Observations
1	M.E.C. $CHCl_3$	20 80	Méthanol $CHCl_3$ HCl conc.	70 20 10	+	+	+			taches séparées
2	id.	id.	id.	id.	+	+	+			pas de séparation
3	$CHCl_3$	100	Acétone $CHCl_3$ HCl conc.	70 20 9	 +	 +	 + +			pas de séparation taches séparées
4	M.E.C. $CHCl_3$	50 50	Acétone $CHCl_3$ HCl conc.	71 20 9	+	+	+			taches séparées
5	id.	id.	id.	id.	+	+	+			taches séparées
6	id.	id.	id.	id.	+			+		V dispersé
7	Alc.amyl. HCl conc. Benzène	60 30 10	Alc.amyl. HCOOH	45 55	+		+			*A/C* *B/C* W -0.00/0.06-0.10 V -0.16/0.12-0.37/37 Cr-0.16/0.17-0.43/38 Mo-0.39/0.32-0.66/56
8	id.	id.	id.	id.	+				+	*A/C* *B/C* W-0.00 -0.05 V-0.13 -0.37 Cr-0.10/11/ -0.34/35 0.12/13 0.36/33 Mo-0.47/49 -0.69/68

PARTIE QUANTITATIVE

I. *Détermination quantitative du vanadium seul en solution*

Toutes les méthodes de dosage du vanadium sont basées sur sa facile oxydabilité et réductibilité[8 à 13].

La plupart des méthodes sont basées sur la titration par le permanganate, après réduction du vanadium, par divers agents comme l'acide sulfhydrique ou l'anhydride sulfureux. Le titrage par le permanganate a été essayé, mais s'est révélé moins sensible que celui adopté par nous.

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1. *Principe*

EVANS[14] a observé que l'addition d'une solution alcoolique de diphénylcarbazide à une solution de nitrate de plomb, en présence de pyridine, provoque une coloration rouge cerise.

Le vanadium(V^{+5}) donne une couleur à peu près identique à celle du plomb. Si l'on ajoute le réactif à une solution neutre de vanadate et que l'on titre par du nitrate de plomb, la coloration s'atténue par suite de la précipitation de vanadate de plomb, jusqu'au moment où subsiste la coloration due à la présence du réactif; un excès de plomb provoque alors l'apparition de la couleur due au plomb.

Ce titrage a été préconisé par EVANS jusqu'à 80 µg de vanadium(V^{+5}). Le vanadium(V^{+4}) ne se prête pas à ce dosage. Une mise au point est donc nécessaire pour titrer des quantités de vanadium de l'ordre de 10 µg.

2. *Réactifs*

1. Une solution à 1.5 g % p/v de diphénylcarbazide dans l'alcool éthylique.
2. Pyridine distillée (produit B.D.H.)-fraction ébullition 115° C.
3. Acide nitrique dilué (densité: 1.2).

Préparation des réactifs

Un réactif six fois plus concentré en diphénylcarbazide que celui utilisé par, Evans est préparé pour obtenir une coloration plus intense.

A un mélange de 2.5 ml de pyridine diluée dans 10 ml d'eau, on ajoute 0.17 ml d'acide nitrique (densité: 1.2) et 5.0 ml de la solution alcoolique de diphénylcarbazide à 1.5 g %. On laisse reposer le réactif pendant deux nuits avant l'emploi, il se conserve alors plusieurs jours.

Test de contrôle de ce réactif

La coloration produite par le vanadium est rouge-cerise, tandis qu'un blanc donne une couleur jaune pâle. L'addition d'acétone accentue la différence des teintes.

3. *Sensibilité du dosage*

La sensibilité du dosage a été étudiée avec une solution quantitative de vanadium contenant 8 µg de vanadium(V^{+5}) par 0.01 ml, et préparée de la manière suivante:

0.183620 g de vanadate d'ammonium (limite de sa solubilité dans ces conditions opératoires), 9.6 g d'acide acétique glacial, 12.8 g d'acétate de sodium, 6 g d'hydroxyde de sodium, le tout porté à 100 ml avec de l'eau bidistillée.

Des volumes différents de cette solution ont été titrés par du nitrate de plomb contenant 1 g par litre.

Les résultats de ces titrages sont consignés dans le tableau ci-après:

TABLEAU IV

Volume prélevé ml	Correspondance en µg de V^{+5}	Volume de $(NO_3)_2Pb$ utilisé ml	Moyenne
0.0100	8.0	0.0618 0.0608	*M*/2 0.0613
0.0105	8.4	0.0600 0.0650 0.0622	*M*/3 0.0626
0.0110	8.8	0.0632 0.0658 0.0635	*M*/3 0.0643
0.0115	9.2	0.0650 0.0651	*M*/2 0.0650
0.0120	9.6	0.0663 0.0665 0.0669 0.0668 0.0668 0.0660 0.0659 0.0668	*M*/8 0.0665
0.0125	10.0	0.0682 0.0683	*M*/2 0.0682
0.0130	10.4	0.0693 0.0695 0.0692 0.0699 0.0688 0.0698	*M*/6 0.0694
0.0135	10.8	0.0705 0.0704	*M*/2 0.0704

II. *Microtitrage du vanadium chromatographié*

1. *Méthode employée*

La révélation qualitative sert de guide pour le découpage des taches chromatographiées de vanadium.*

Ces taches sont laissées une heure dans une atmosphère saturée d'ammoniac afin d'oxyder le vanadium, partiellement réduit en vanadium(V^{+4}) par le papier, au cours du processus chromatographique. En effet, le vanadium(V^{+4}) non titrable directement, s'oxyde rapidement à l'air en milieu alcalin. Il ne semble pas qu'un séjour prolongé des bandelettes dans l'atmosphère d'ammoniac soit favorable.

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* Voir page 446, préparation de l'oxine acétique employée comme révélateur.

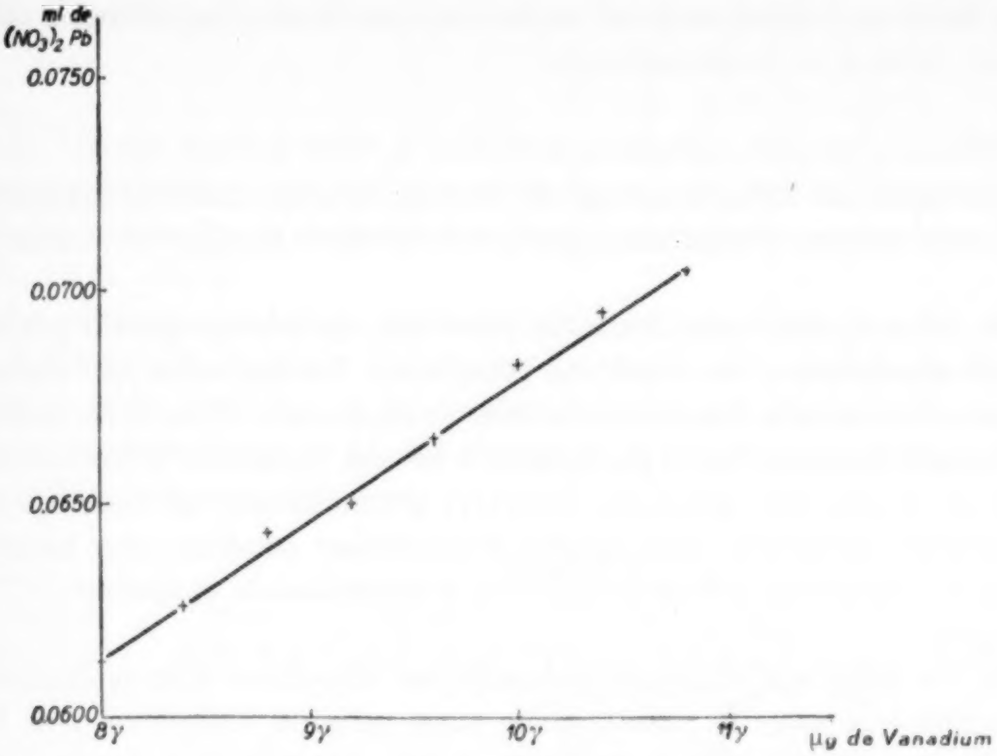

Fig. 1. Sensibilité du dosage du vanadium.

Le titrage ne réussit qu'en solution neutre; or, les bandelettes chromatographiées sont à un pH différent de la neutralité, selon la nature de la solution de départ, du développant et du saturant. Le séjour en ammoniac ne suffit pas dans tous les cas pour obtenir cette neutralité nécessaire. C'est pourquoi il a fallu trouver une solution réajustant le pH. L'acide borique, le borax, l'acétate d'ammonium, l'acétate de sodium, le chlorure d'ammonium ont été essayés, mais c'est la pyridine mélangée à l'eau nitrique qui conduit au but, — que la prise soit chlorhydrique, acétique, chlorhydrique-acétique, acétique-sodique-acétate de sodium.

La bandelette est placée, roulée, dans un godet de forme haute en verre blanc (diamètre 2 cm, hauteur 5 cm). On y ajoute 4.5 ml d'eau bidistillée et 0.5 ml d'une solution de pyridine dans de l'eau nitrique préparée comme suit: 85 ml d'eau, 14 ml de pyridine distillée et 1 ml d'acide nitrique (densité: 1.42). On ajoute ensuite 0.5 ml du réactif à la diphénylcarbazide et 3.0 ml d'acétone. La solution est alors rose amarante; on titre par une solution de nitrate de plomb à 1 g par litre à l'aide d'une microburette horizontale de 0.1 ml (permettant d'apprécier le 0.0001 ml) jusqu'à décoloration de la solution.

Une référence de 10 μg de vanadium est d'abord dosée par comparaison avec un essai à blanc. Ce dernier contient les mêmes produits, moins la prise de vanadium. Ensuite, on dose les bandelettes par rapport à la référence. Le titrage est effectué en lumière blanche, les colorations dans les godets sont observées sur fond et écran blancs. L'agitation de la solution pendant l'addition de nitrate de plomb est réalisée par barbotage d'azote.

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L'addition des derniers centièmes de ml se fait en une dizaine de minutes, car la décoloration est lente à ce moment.

2. *Résultats obtenus*

Les résultats obtenus en dosant 10 µg de vanadium non chromatographié sont concluants: aux erreurs d'expérience près, on retrouve la quantité initiale prélevée.

Le titrage a été mis au point ensuite sur du *vanadium chromatographié* à partir d'une solution chlorhydrique. Les résultats étant trop faibles, nous en avons déduit qu'une partie du vanadium avait été réduite par le papier. Pour le *réoxyder*, plusieurs méthodes ont été essayées: le perhydrol, le brome, l'addition d'ammoniac par voie humide et à sec. Les meilleurs résultats sont obtenus en laissant le vanadium se réoxyder dans une atmosphère d'ammoniac pendant une heure. Le titrage doit suivre assez rapidement pour éviter la réduction du vanadium(V^{+5}) à l'air, par le papier.

D'après EVANS, les solutions citriques et tartriques détruisent non seulement la coloration du complexe avec le plomb, mais aussi celle du complexe avec le vanadium. Nous avons vérifié le fait pour des taches de vanadium provenant d'une solution tartrique. Le vanadium(V^{+5}) chromatographié est accompagné de tartrates et ces taches ne sont pas titrables par la méthode d'EVANS.

3. *Reproductibilité du titrage du vanadium*

La reproductibilité a été étudiée sur des taches de vanadium provenant de prises différentes: solutions acétique-chlorhydrique, chlorhydrique et acétique-acétate de sodium-sodique.

Le dosage du vanadium se fait avec une précision qui est au moins aussi bonne que celle obtenue par colorimétrie pour des quantités de vanadium (V^{+5}) de l'ordre de 10 µg.

TABLEAU V

Nature de la prise	Volume de $(NO_3)_2Pb$ nécessaire pour titrer la référence ml	µg de V^{+5} mis en œuvre	Titrage des taches chromatographiées				
			$(NO_3)_2Pb$, ml		Moyenne en ml	Moyenne en µg	Erreurs % en µg
HAc-HCl	0.0652	9.20	0.0650/665/651/651	$M/4$	0.0654	9.26	+0.6 %
HAc-AcNa-NaOH	0.0685	10.20	0.0671/672/669/672 678/686/696/673 670/672	$M/10$	0.0676	9.94	—2.54%
HCl 10%	0.0730	11.60	0.0766/770/742/740 760/750	$M/6$	0.0754	12.36	+6.14%

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III. *Contrôle quantitatif des séparations chromatographiques qualitatives vanadium-molybdène*

Le titrage nous a servi à contrôler la marche des séparations. C'est ainsi que des séparations paraissant quantitatives se sont révélées imparfaites par suite de la présence de traces de molybdène dans le vanadium et vice-versa (voir expérience No. 16 p. 682-7).

Le principe du dosage du molybdène est semblable à celui du vanadium. Le molybdène est titré par du nitrate de plomb en présence de diphénylcarbazide comme indicateur. Un excès de nitrate de plomb provoque la coloration de l'indicateur et indique la fin du titrage. Les résultats quantitatifs sont consignés dans les tableaux suivantes:

TABLEAU VI

p. o.	Prises p.s.	 p.n.s.	V^{+5} *A/C B/C*	Mo^{+6} *A/C B/C*	Vanadium Titrage $(NO_3)_2Pb$ ml	[Référence: 9.97 μg] Retrouvé μg	 Erreur μg	Molybdène Titrage $(NO_3)_2Pb$ ml	[Référence: 9.98 μg] Retrouvé μg	 Erreur μg
1	+		0.16-0.57	0.72-1.00	0.0702	10.00	+0.3	0.0357	*M*/2	
49					0.0678			0.0358	10.08	+1.0
6	+		0.20-0.63	0.69-1.00	0.0686	*M*/2		0.0373		
50		+			0.0696	10.40	+4.3	0.0378	10.42	+5.0
			0.19-0.61	0.61-1.00	0.0672	*M*/2				
					0.0670	9.78	—1.9			
7	+		0.24-0.65	0.79-1.00	0.0630	8.52 (!)				
50										
8					*M*/4			*M*/4		
50	+		0.25-0.64	0.75-1.00	0.0676	9.94	—0.3	0.0413	11.3 (!)	
8	+		0.20-0.58	0.80-1.00	0.0658					
50					0.0622	Résultat décroissant avec le temps, car il y a réduction progressive au cours de l'attente des godets à titrer.				
					0.0592					
		+	0.25-0.57	0.80-1.00	0.0644					
					0.0638					
					0.0579					
					Référence: 10.00 μg			Référence: 9.99 μg		
	+		0.22-0.55	0.70-1.00	0.0682	*M*/3		0.0332	*M*/2	
50					0.0638	9.50	—4.7	0.0312	9.56	—4.2
					0.0665					
		+	0.20-0.55	0.70-1.00	0.0642	8.90 (!)		0.0349	*M*/2	
								0.0335	9.94	—0.3
	+		0.10-0.39	0.75-1.00	0.0650					
50					0.0652					
					0.0680	*M*/4				
					0.0665	9.50	—4.7			

. = prises séchées 10′ I.R. 35-38° C avant chromatographie.

.s. = prises chromatographiées humides.

= Séparation non quantitative.

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IV. *Avantages du titrage direct sur papier*

Le dosage dans ces conditions est très simple, il ne nécessite pas de matérial coûteux ni de montage compliqué, de plus il est rapide et automatique pour une grande partie. Le titrage a lieu immédiatement après la séparation chromatographique. Nous éliminons ainsi l'élution, ce qui raccourcit de 3 heures les opérations de dosage du molybdène.

La nécessité de passer les bandelettes à l'ammoniac, afin de réoxyder le vanadium, montre que le papier, contrairement à ce que pensent certains auteurs, n'est pas un élément inerte en chromatographie; ce support réducteur agit sur le vanadium.

Le titrage mis au point ici permet de mettre en évidence que les complexes tartrique et acétique du vanadium migrent dans le papier comme un seul élément, en entraînant avec eux le vanadium.

REMERCIEMENTS

Cette recherche n'a pu se faire que grâce à un subside du Fonds National de la Recherche Scientifique. Nous exprimons ici notre gratitude au Comité Directeur de cette Institution.

RÉSUMÉ

La présente recherche précise le comportement qualitatif du molybdène et du vanadium lorsqu'ils sont chromatographiés en mélange sur papier.

Les recherches ont porté sur des solutions de départ de natures différentes; elles ont abouti à des séparations qualitativement très intéressantes. Le contrôle quantitatif de ces séparations a été fait par titration directe de la tache d'élément sur la bandelette chromatographiée.

Cette technique accélère tout le processus, sans rien enlever à la précision des déterminations.

SUMMARY

Chromatographic behaviour on paper of molybdenum and vanadium when mixed in the same solution has been studied. Very good qualitative separations have been found for both elements.

Quantitative control of these separations has been checked by direct titration of the chromatographed spot on the paper.

This technique speeds the whole procedure very much without harming in any way the accuracy of the determinations.

ZUSAMMENFASSUNG

In der vorliegenden Untersuchung wurde das qualitative Verhalten von Molybden-Vanadingemengen bei der Papierchromatographie genau untersucht. Die Untersuchungen wurden mit Ausgangslösungen verschiedener Natur durchgeführt.

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Sie haben zu sehr interessanten qualitativen Trennungen geführt. Die quantitative Kontrolle dieser Trennungen wurde durch direkte Titration der Tüpfel dieser Elemente auf chromatographischen Streifen durchgeführt.

Diese Technik beschleunigt das gesamte Verfahren, ohne die Genauigkeit der Bestimmung zu beeinträchtigen.

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PHOTOMETRIC MEASUREMENTS OF IRON OXALATES

by

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A photometric and spectrophotometric study of the iron oxalate complexes: 1 Fe^{III}/1 Ox and 1 Fe^{III}/3 Ox was made. A method is presented here for a quick standardization of solutions of iron with oxalate or vice versa. In addition, a method was developed for an accurate photometric determination of traces of iron with the aid of oxalate, or traces of oxalate with the aid of iron in presence of thiocyanate. All the above determinations require only a primary solution of weighed oxalate.

The oxalate complexes have been known since the time of WERNER. Most of the cations give oxalate complexes of the general formula $[M^n(C_2O_4)_3]\ R_{6-n}$. It is assumed that in these complexes the coordination number is 6, and their octahedral structure makes optical isomerism possible[1, 15].

Among the trivalent elements, only 13 cations are known which give complexe. of the type $[M(C_2O_4)_3]^{-3}$. Among these are: V, Cr, Mn, Fe, Ru, Co, Rh, Ir, and Als The existence of optical isomerism was proved only in the cases of Cr, Co, Rh and Ir.

Experiments have been made on the optical separation of the oxalate complexes by DELEPINE.

The quick racemization in the case of iron and aluminium oxalate was explained by the following equilibrium (4):

$$\begin{array}{ccccc} d[M(C_2O_4)_3]^{-3} & \rightleftarrows & [M(C_2O_4)_2]^{-1} + C_2O_4^{-2} & \rightleftarrows & dl[M(C_2O_4)_3]^{-3} \\ \text{octahedral} & & \text{planar, symmetrical} & & \text{raceme} \end{array}$$

The oxalate complexes of iron were studied by a polarographic method by TOROPOVA, STACKELBERG-FREYHOLD AND LINGANE.

EXPERIMENTAL DETAILS

Reagents. Analytically pure Baker reagents were used.

Equipment. The photometric titrations were made with a photoelectric titrophotometer built in our laboratory. The light passes vertically through the solution, the filters and the diaphragms and falls on a photoelectric cell. The latter is connected with a sensitive micro-amperemeter. The initial volume of the titrated solution is 20 ml and the diameter of the container cell 4.8 cm. The initial thickness of the layer is about 1.1 cm.

The advantage of this apparatus is that no correction for the increase of thickness is necessary, since the increase of the layer of solution increases the extinction, but at the same time, the dilution also increases. Assuming that the container cell is a perfect cylinder, the above effects can be eliminated and a correction is unnecessary.

The measurements with Corning small pass band filters were made with the aid of a sensitive Leeds and Northrup spot galvanometer No. 2430 of 100 divisions. The measurements with Fisher regular filters were made with the aid of a Cambridge spot galvanometer with 160 mm scale. In the latter, one microampere gave a deflection of 170 mm. With the aid of potentiometers in the apparatus, it was possible to decrease the sensitivity of the galvanometers as desired.

In addition to the titrophotometer we used a Hellige Pan-photometer and a Coleman Universal spectrophotometer. The spectra of iron oxalate and of iron thiocyanate were measured by a Beckman D.U. spectrophotometer. pH measurements were made with a Hellige pH-meter of reading accuracy ± 0.05 pH.

Titrations of iron and oxalate

The composition of the various experiments is shown in Fig. 1. Curves 1, 2 and 3 were obtained from data of photometric titrations, with a Fisher blue filter $\lambda=400$-450. Curve 4 was drawn from titrations with a Corning small band-pass filter of $\lambda = 430$, and curve 5 was drawn from titrations with a Corning small band-pass filter of $\lambda = 460$. The first complex had the relation 1 $\mathrm{Fe^{III}}$/1 Ox and was dark yellow in colour; the second had the relation 1 $\mathrm{Fe^{III}}$/3 Ox and was bright green. The first maximum point could be determined with great accuracy by calculation of a maximum from $\frac{\mathrm{d}E}{\mathrm{d}V} = 0$. The second point 1 $\mathrm{Fe^{III}}$/3 Ox could be obtained by extrapolation from the curves drawn from the values of the extinctions of the individual curves. Fig. 2 (curves 1, 2 and 3), gives us the spectra of the above two complexes as were obtained by us in measurements with a Beckman spectrophotometer. It becomes obvious that there is little difference in the spectra of the above complexes. Since the above spectra did not show a maximum in the visible spectrum, there is no characteristic filter

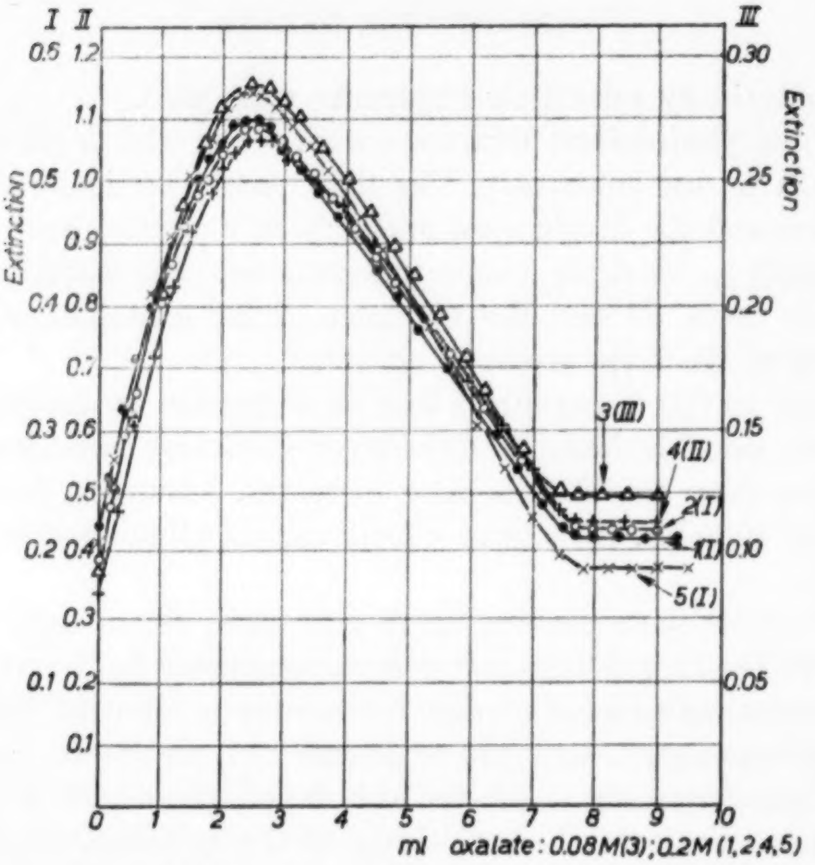

Fig. 1. Titration curves of iron with oxalate

1. 5 ml $FeCl_3$ 0.1 M + 15 ml H_2O + x ml Na_2Ox 0.2 M (Blue filter Fisher, 400-450).
2. 5 ml $FeCl_3$ 0.1 M (HCl 0.01 N) + 15 ml H_2O + x ml Na_2Ox 0.2 M (Blue filter Fisher 400-450).
3. 20 ml $FeCl_3$ 0.01 M + x ml Na_2Ox 0.1 M (Blue filter Fisher, 400-450).
4. 5 ml $FeCl_3$ 0.1 M + 15 ml H_2O + x ml Na_2Ox 0.2 M. (Corning monochromatic 430).
5. 5 ml $FeCl_3$ 0.1 M + 15 ml H_2O + x ml Na_2Ox 0.2 M. (Corning monochromatic 460).

for the photometric titration, and the results with the various filters are analogous.

In order to determine in which concentration range the maxima and minima of the above complexes can serve as good end-points in a titration, photometric titrations were made with a blue filter λ = 400-450. Results are given in Fig. 3. We note that titration with oxalate 0.01 M creates a sharp plateau instead of a sharp maximum. This shows the significance of the *concentration* of oxalate in these titrations, and apparently it will be impossible in these direct titrations to determine *traces* of oxalate or iron (compare below). Fig. 4 shows the results of back titrations: $aC_2O_4^{-2}$ + xFe made with a blue filter (λ = 400-450). A break is obtained with 1 Fe^{III}/3 Ox, but none is obtained with 1 Fe^{III}/1 Ox. This may be due to the disturbances caused by $FeCl_3$ itself.

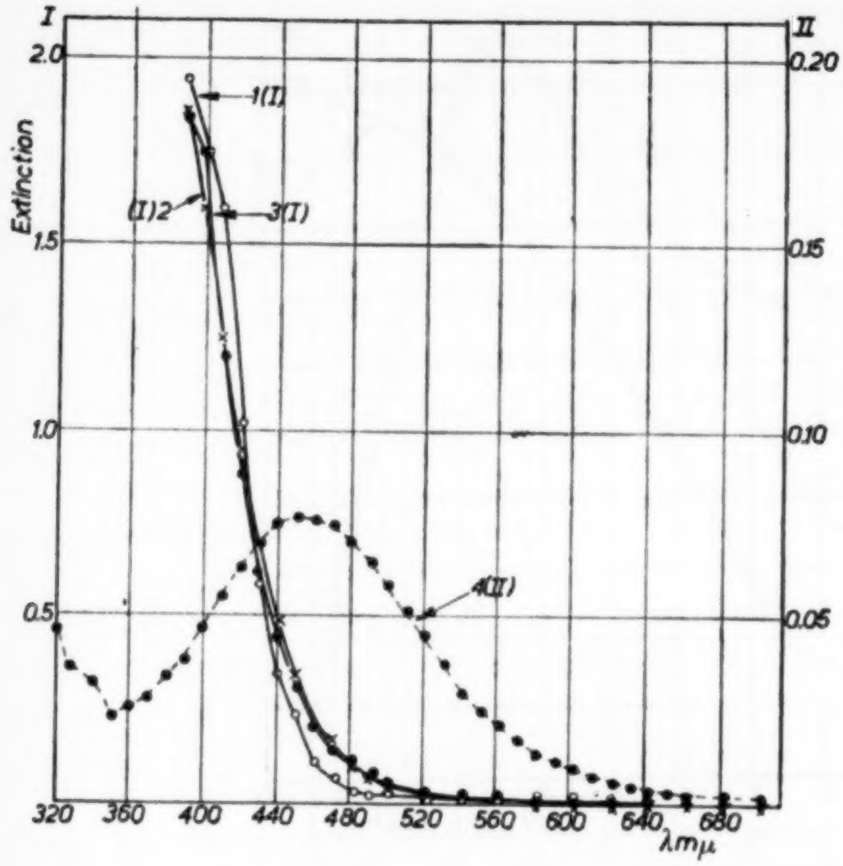

Fig. 2. Spectrophotometric extinction curves

1. 1Fe/1Ox.
   2 ml $FeCl_3$ 0.1 *M* +
   + 2 ml Na_2Ox 0.1 *M* +
   + 16 ml H_2O.
2. 1Fe/1Ox.
   2 ml $FeCl_3$ 0.1 *M*
   (HCl 0.5 *N*) +
   + 2 ml Na_2Ox 0.1 *M* +
   + 16 ml H_2O.
3. 1Fe/3Ox.
   5 ml $FeCl_3$ 0.1 *M*
   (HCl 0.01 *N*) +
   + 15 ml Na_2Ox 0.1 *M*.
4. 10 ml $FeCl_3$ 0.001 *M*
   (HCl 0.1 *N*) +
   10 ml NH_4CNS 0.01 *M*.

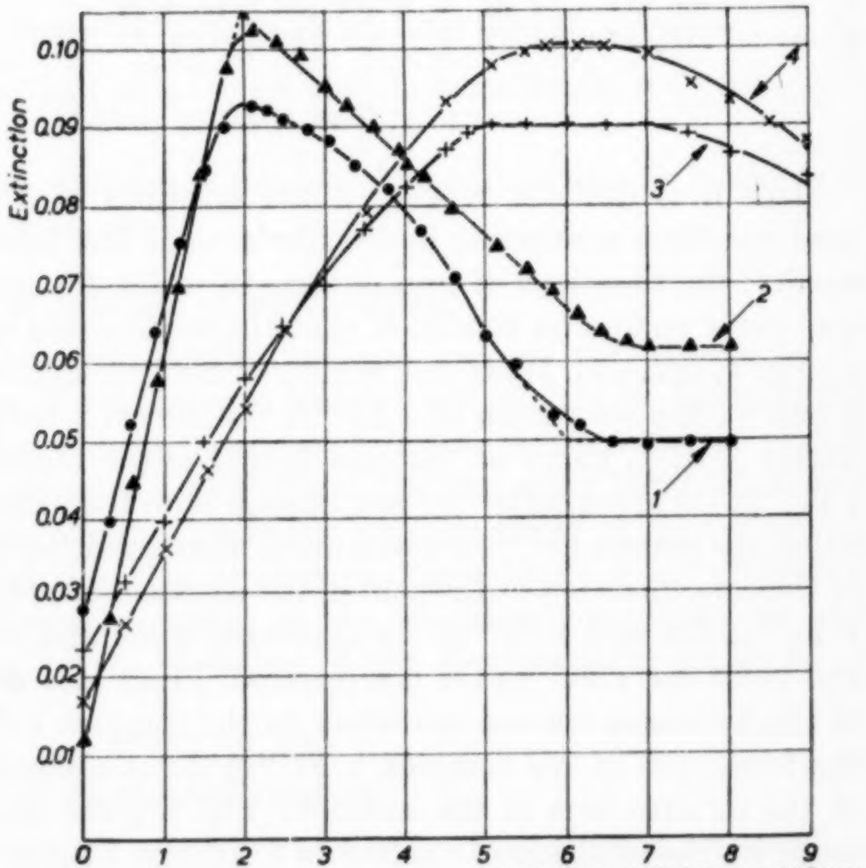

Fig. 3. Titration curves of iron with oxalate (Blue filter Fisher 400-450)

1. 5 ml $FeCl_3$ 0.01 *M* +
   + 15 ml H_2O +
   + x ml Na_2Ox 0.025 *M*.
2. 5 ml $FeCl_3$ 0.01 *M*
   (HCl 0.02 *M*) +
   + 15 ml H_2O +
   + x ml Na_2Ox 0.025 *N*.
3. 5 ml $FeCl_3$ 0.01 *M*
   + 15 ml H_2O +
   + x ml Na_2Ox 0.01 *M*.
4. 5 ml $FeCl_3$ 0.01 *M*
   (HCl 0.02 *N*) +
   + 15 ml H_2O +
   + x ml Na_2Ox 0.01 *M*.

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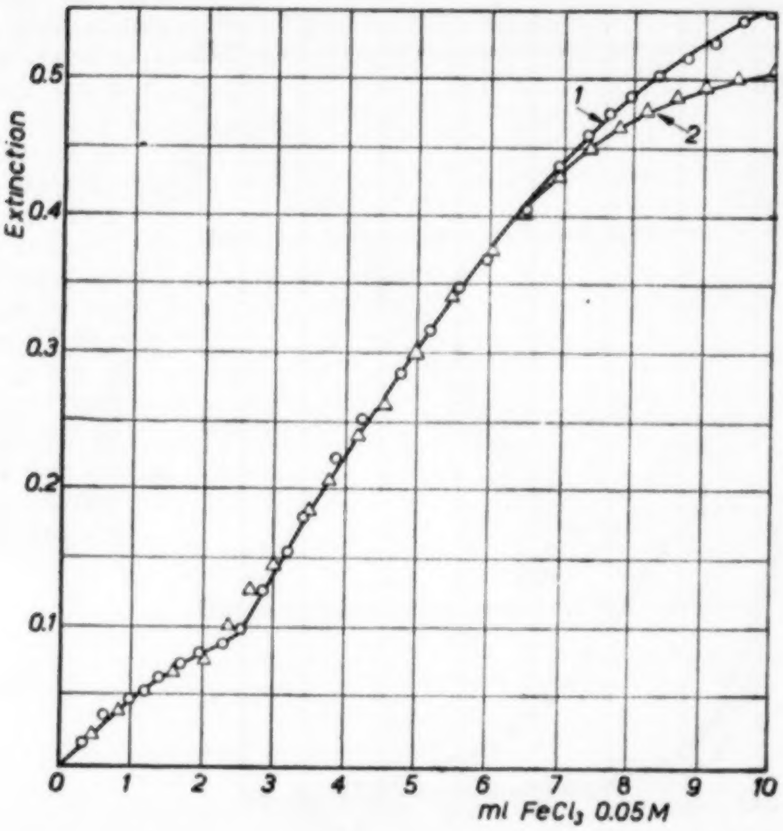

Fig. 4. Titration curves of oxalate with iron (Blue filter Fisher 400-450)
1. 20 ml Na_2Ox 0.02 *M* + x ml $FeCl_3$ 0.05 *M*.
2. 20 ml Na_2Ox 0.02 *M* + x ml $FeCl_3$ 0.05 *M* (HCl 0.05 *N*).

The effect of acidity

Since it is difficult to keep dilute solutions of iron chloride in solution, we used solutions containing hydrochloric acid. The following is a summary of the results: the titrations of iron oxalate in which the iron solution was acidic gave the above results on condition that the acidity was not great, (see Fig. 1, curve 2; Fig. 5, curve 1). When the acidity of the iron solution increased (Fig. 5, curves 2 and 3), the maximum of 1 Fe^{III}/1 Ox moved a little to the right and became flatter (Fig. 5, curve 2), but the height of the maximum obtained at the point 1 Fe^{III}/1 Ox apparently did not change with the increase in acidity. On the other hand, the point 1 Fe^{III}/3 Ox was much more sensitive to acidity. With the increase of the concentration of the acid in the solution, the extinction between the points 1 Fe^{III}/1 Ox and 1 Fe^{III}/3 Ox decreased more and more slowly, and a suitable end-point for 1 Fe^{III}/3 Ox disappeared. From this we learn that the influence of the hydrogen ion concentration on the complex 1 Fe^{III}/1 Ox is small and that the formation of the complex 1 Fe^{III}/3 Ox is connected with the concentration of the oxalate ions in the solution. Fig. 6 gives the pH curve of the titration made by the addition of oxalate to a solution of iron chloride. The titration was begun at a very low pH and for some time the pH remained constant. It then

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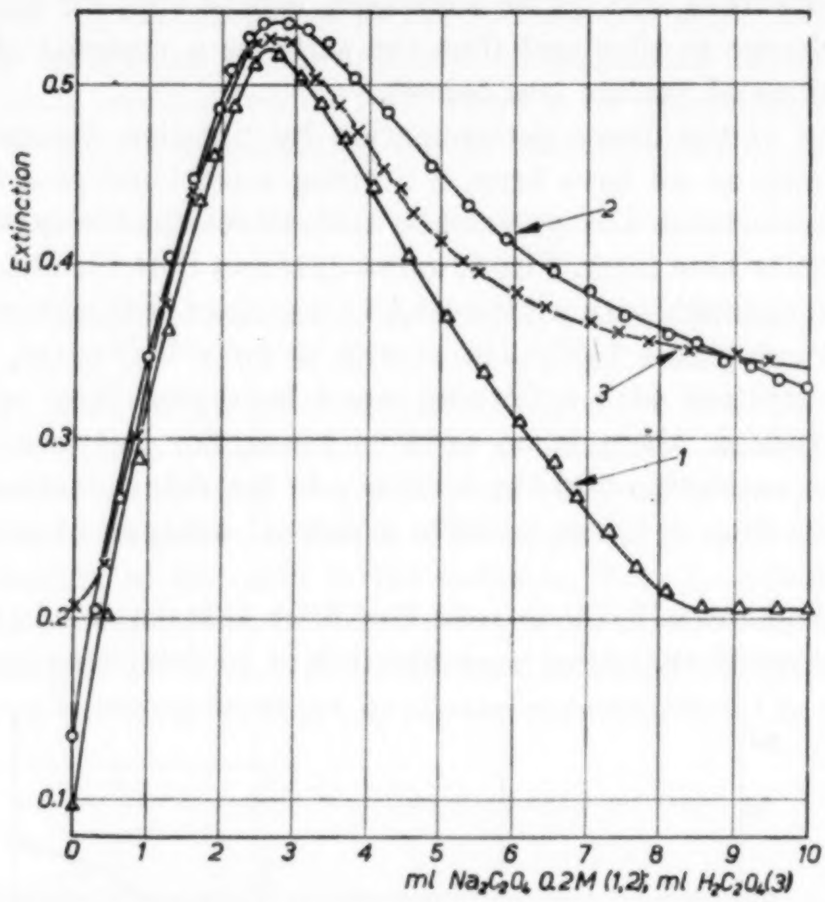

Fig. 5. Titration curves of iron with oxalate (Blue filter Fisher 400-450)
1. 5 ml $FeCl_3$ 0.1 *M* (HCl 0.05 *N*) + 15 ml H_2O + x ml Na_2Ox 0.2 *M*.
2. 5 ml $FeCl_3$ 0.1 *M* + 5 ml HCl *N* + 10 ml H_2O + x ml Na_2Ox 0.2 *M*.
3. 5 ml $FeCl_3$ 0.1 *M* + 15 ml H_2O + x ml H_2Ox 0.2 *M*.

increased gradually with the addition of oxalate. The end-point was in the area of 1 Fe^{III}/3 Ox when the pH reached 7.

The structure of the complexes

From the above curves we can deduce the existence of two complexes, 1 Fe^{III}/1 Ox and 1 Fe^{III}/3 Ox. From other studies of iron oxalate we know of the existence of three complexes, among them 1 Fe^{III}/2 Ox. Apparently its photometric properties resemble those of 1 Fe^{III}/3 Ox. On the other hand, we found that it was possible to obtain quantitatively the complex 1 Fe^{III}/3 Ox by adding to 1 Fe^{III}/1 Ox a calculated quantity of oxalate. Since there is no difference in the function of the individual oxalates in the trioxalate complexes, we can attribute a particular value to the structure of the mono-oxalate complex.

ANALYTIC USE

Photometric titration

The above titrations can be used as a quick and convenient method for standardization of solutions of iron salts containing free HCl of about 0.02 *N* in solution.

These acid solutions of iron, as we have seen, can be kept for an unlimited time without any change in titer and thus can serve as a material of constant titer for determinations of oxalate (see below).

The accuracy of the direct determination by titration depends on the layer of absorption and, as we have been, a Corning small band-pass filter of a short wave-length (for instance $\lambda = 430$) can be used, increasing the extinction obtained by use of a regular blue filter. Fig. 1, curve 4, shows that the absolute extinction is almost twice as much with a filter of $\lambda = 430$ than with one of $\lambda = 460$. This is true for the complex 1 Fe^{III}/1 Ox as well as for 1 Fe^{III}/3 Ox, and this is the advantage of titration with a Corning small band-pass filter of $\lambda = 430$ (see also Fig. 2). Indeed, there is no obvious connection between the magnitude of difference in extinction and the accuracy in the determination of the points. The two points (Fig. 1) make possible a mutual analysis of one point against the other.

By this method and with the use of a blue filter, it is possible to titrate solutions of iron salts of usual analytical concentration or to determine oxalic acid in the

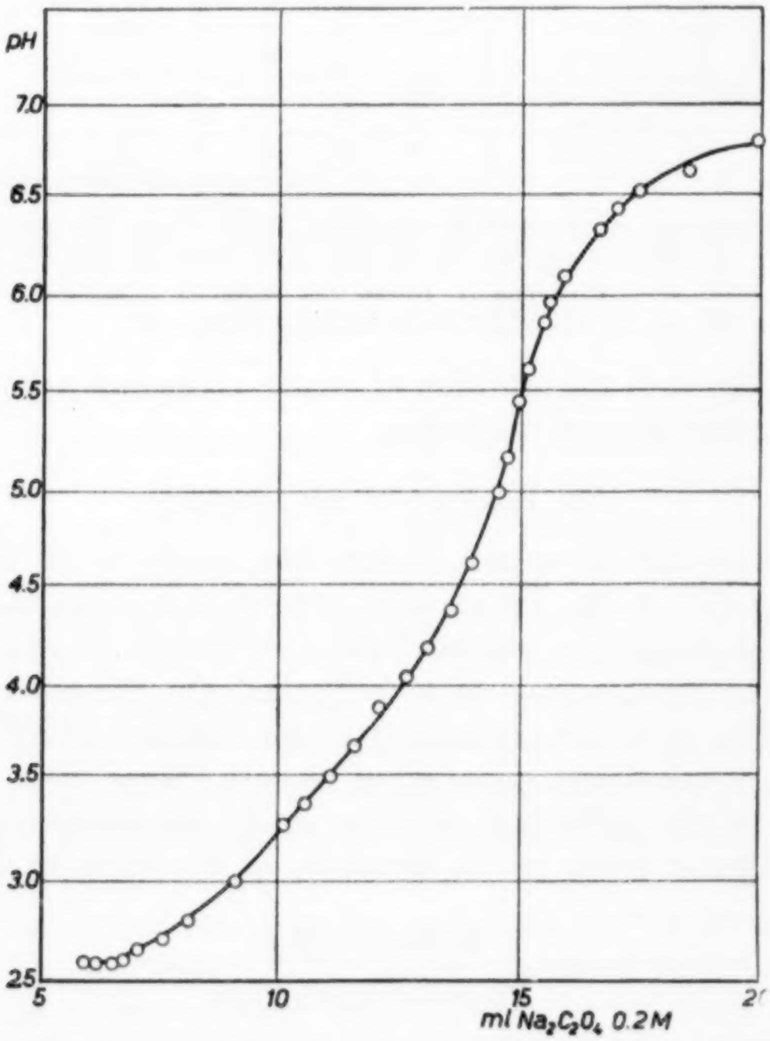

Fig. 6. pH titration curve of iron with oxalate
10 ml $FeCl_3$ 0.1 M + 10 ml H_2O + x ml Na_2Ox 0.2 M

presence of other organic materials in the solution (on condition that they do not give strong complexes with iron). The concentration of the iron solution should not decrease much below 0.01 N. There is no difficulty, however, in the determination of solutions containing higher concentration of iron.

Photometric determinations of traces of iron or traces of oxalate in the presence of thiocyanate

When dilute solutions of iron are titrated with oxalate in the presence of thiocyanate, the color of the latter is destroyed gradually and we obtain a yellow solution (Fig. 7) and then a green solution. When the extinction is measured during the titration with a Fisher blue filter or a Corning small band-pass green filter, curves, each consisting of two parts, are obtained (Fig. 7). The first part, sensitive to traces of oxalate, is linear. The length of this linear part depends on the concentration of the acid in the solution (Fig. 5, curves 1-5). Various quantities of HCl were added to solutions of iron chloride in order to obtain the final normality of the acid. The concentration of the thiocyanate in the original solution (see below) is constant in all the experiments. (The determinations

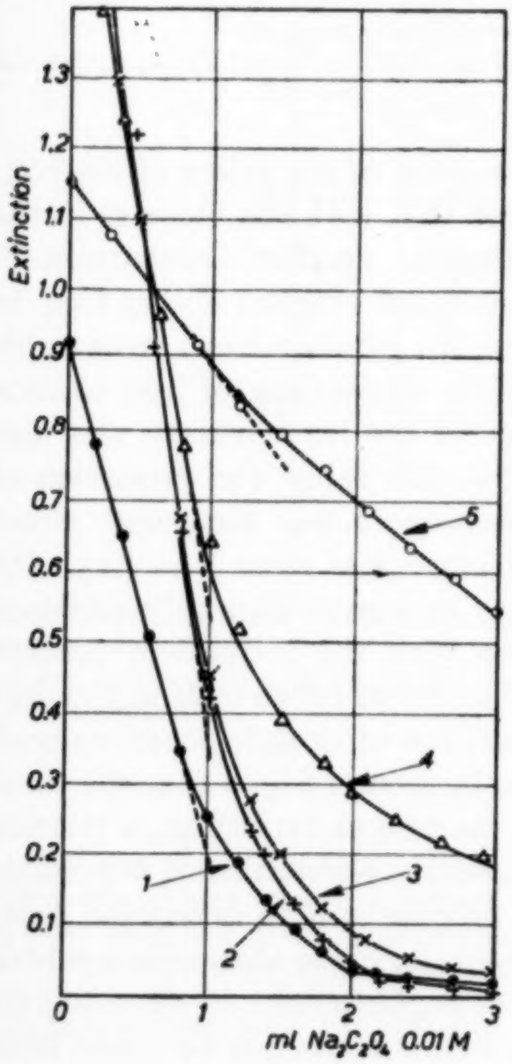

Fig. 7. Titration curves of iron with oxalate in the presence of thiocyanate (Green Corning monochromatic filter $\lambda = 515$)

1. 5 ml $FeCl_3$ 0.002 M + 5 ml NH_4CNS 0.1 M + 10 ml H_2O + x ml Na_2Ox 0.01 M.
2. 5 ml $FeCl_3$ 0.002 M (HCl 0.01 N) + 5 ml NH_4CNS 0.1 M + 10 ml H_2O + x ml Na_2Ox 0.01 M.
3. 5 ml $FeCl_3$ 0.002 M (HCl 0.01 N) + 5 ml NH_4CNS 0.1 M + 1.5 ml HCl 0.1 N + 8.5 ml H_2O + x ml Na_2Ox 0.01 M.
4. 5 ml $FeCl_3$ 0.002 M (HCl 0.01 N) + 5 ml NH_4CNS 0.1 M + 1.5 ml HCl N + x ml Na_2Ox 0.01 M.
5. 5 ml $FeCl_3$ 0.002 M (HCl 0.01 N) + 5 ml NH_4CNS 0.1 M + 5 ml HCl N + 5 ml H_2O + x ml Na_2Ox 0.01 M.

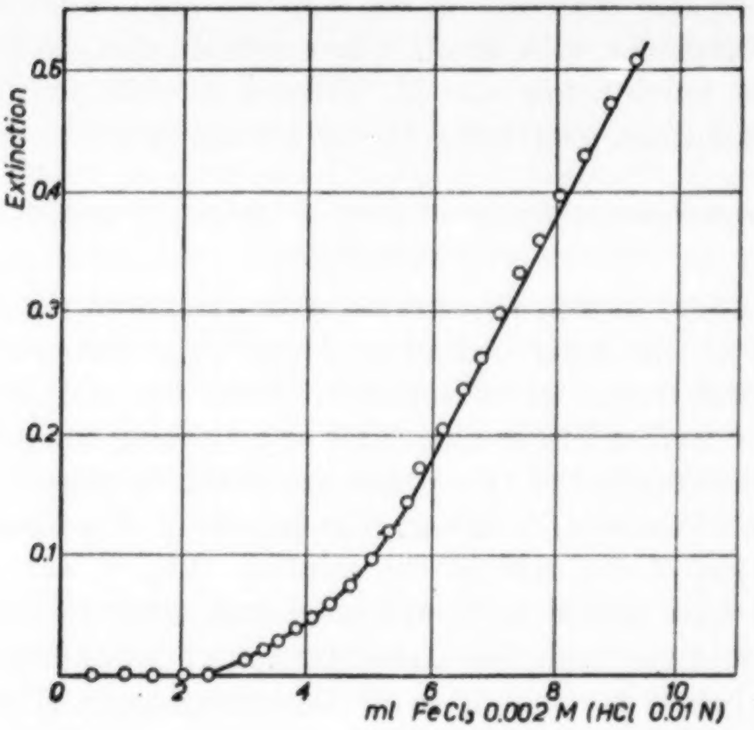

Fig. 8. Titration curve of oxalate with iron (Green filter 500-540)
5 ml Na_2Ox 0.002 *M* + 2 ml NH_4CNS 0.05 *M* + 13 ml H_2O + x ml $FeCl_3$ 0.002 *M* (HCl 0.01 *N*)

were first made by a blue filter λ = 400-450.) Analysis of the effect of the concentration of thiocyanate with a blue filter showed that with the increase in the concentration of the thiocyanate, the extinction was greater. Comparison of the absorption spectra of iron oxalate and thiocyanate (Fig. 2) shows that in this range, an iron oxalate complex obtained during the titration has a measurable extinction so that with a blue filter, the *sum* of the extinctions of iron oxalate and iron thiocyanate were measured. The effect of the iron oxalate was also measured with a green filter λ = 500-540 since in this range the extinction of iron oxalate was equal to zero, and the iron thiocyanate was measured alone. The titrations were made with a Corning small band-pass filter λ = 515. The composition of the experiments and the results can be seen in Fig. 7. In all cases, the length of the linear part of the curve decreases with the increase in concentration of the acid of the iron chloride solution. The linear curve ends in the area of 1 Fe^{III}/1 Ox. Results are also given of back titrations of oxalate solutions with iron made with a green filter, λ = 500-540. It can be seen in Fig. 8 that the titration curve is a straight line. By extrapolation to the zero of extinction, a relation close to 1 Fe^{III}/1 Ox is obtained. The longest linear curve shows that it is possible to titrate dilute solutions of less than 0.001 *M* oxalate and to determine these solutions photometrically in the presence of thiocyanate. Fig. 9 shows photometric measurements made with a Coleman Universal Spectrophotometer in wave-lengths (1) 490, (2) 520, (3) 550. The composition of the experiments can be taken from the figure. All three curves are linear throughout, but the sensitivity of the measurement increases if a shorter wave-length is used.

As can be seen, it is possible by this photometric method, to determine traces of iron or oxalate in a solution, with an accuracy of about 1%. From the above experiments, the following method was obtained:

To every 13 ml of a neutral solution of oxalate (containing 2-3 mg oxalic acid in 100 ml liquid), 5 ml of a standard iron chloride solution 0.002 *M* (containing HCl 0.01 *M*), and 2 ml of an NH_4CNS 0.06 *M* solution are added. The extinction is measured with a green filter, and the quantity of oxalate is obtained from a empirical curve. The accuracy of the determination is within the limits of 1%. In the direct photometric titration (without thiocyanate), *calibrated curves are unnecessary*, but the sensitivity is at most ten times smaller.

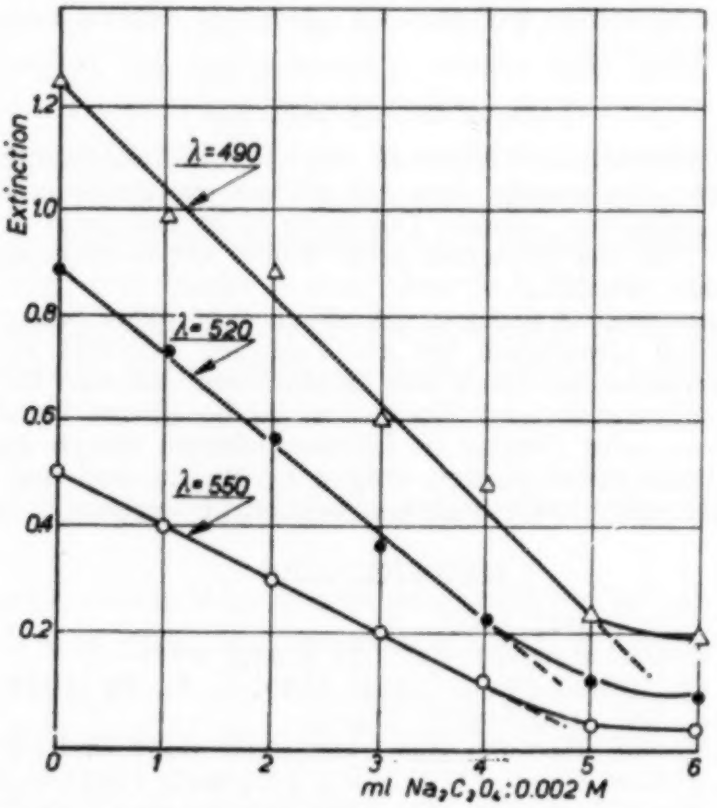

Fig. 9. Extinction curves of iron with oxalate in the presence of NH_4CNS (Coleman Spectrophotometer)
5 ml $FeCl_3$ 0.002 *M* (HCl 0.01 *N*) + 2 ml NH_4CNS 0.05 *M* + (13-x) ml H_2O + x ml Na_2Ox 0.002 *M*.

SUMMARY

1. By the photometric titration of solutions of ferric iron with sodium oxalate using a blue filter, two complexes, 1 Fe^{III}/ 1 Ox and 1 Fe^{III}/3 Ox, could be detected. The first complex gives a maximum point and the second a minimum point. No sign of the existence of a complex, 1 Fe^{III}/2 Ox, could be traced photometrically.

2. The complex 1 Fe^{III}/1 Ox is not sensitive to acids, but the complex 1 Fe^{III}/3 Ox is gradually destroyed by growing acidity.

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3. Both ferric iron and the oxalate ion can be determined in solutions by the above maximum and minimum points.

4. Traces of iron or of oxalate in solution can be determined photometrically with precision by adding definite quantities of thiocyanate to the above solutions and by using a green filter.

RÉSUMÉ

1. Par titration photométrique (avec filtre bleu) des solutions de fer(III) au moyen d'oxalate de sodium, deux complexes, 1 Fe^{III}/1 Ox et 1 Fe^{III}/3 Ox, peuvent être mis en évidence. Le premier complexe donne un point maximum et le second, un point minimum. On ne constate pas par photométrie l'existence d'un complexe 1 Fe^{III}/2 Ox.

2. Le complexe 1 Fe^{III}/1 Ox n'est pas sensible aux acides, mais 1 Fe^{III}/3 Ox est détruit graduellement, au fur et à mesure que l'on augmente l'acidité.

3. Soit le fer^{III}, soit l'anion oxalique, peuvent être décelés dans des solutions par les points maximum et minimum.

4. Des traces de fer ou d'oxalate en solution peuvent être déterminées photométriquement avec précision en présence de quantités déterminées de thiocyanate et en utilisant un filtre vert.

ZUSAMMENFASSUNG

1. Bei der photometrischen Titration von Ferriionenlösungen mit Natriumoxalat konnten bei der Benützung eines Blaufilters ein Fe^{III}/Ox-Komplex und ein Fe^{III}/3 Ox-Komplex gefunden werden. Der erste Komplex zeigt ein Maximum, der zweite ein Minimum. Für das Bestehen eines Fe/^{III}2 Ox-Komplexes konnten keine Anzeichen aufgefunden werden.

2. Der Fe^{III}/Ox-Komplex ist nicht empfindlich gegenüber Säuren, dagegen wird der Fe^{III}/3 Ox-Komplex allmählich bei ansteigender Acidität zerstört.

3. Sowohl die Ferriionen als auch die Oxalationen können in Lösungen durch die oben erwähnten Maximal- und Minimalwerte bestimmt werden.

4. Spuren von Eisen oder Oxalat in Lösung können durch Hinzufügung einer bestimmten Menge Thiocyanat zu den obigen Lösungen und der Benützung eines Grünfilters photometrisch mit Genauigkeit bestimmt werden.

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INFLUENCE DES RÉACTIONS CHIMIQUES PRÉALABLES SUR LA FORME DES COURBES DE POLARISATION

par

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Lorsqu'un oxydant (ou un réducteur) existe sous deux formes en équilibre dans une solution, on constate que la courbe de polarisation peut prendre des formes variées selon la vitesse avec laquelle cet équilibre se réalise dans la couche de solution au contact de l'électrode. Lorsque la réaction chimique est lente on observe deux vagues successives („vagues cinétiques").

Différents auteurs ont étudié la variation de la densité de courant limite de la première vague en fonction des constantes de vitesse de la réaction chimique[1 à 4]. Nous nous proposons ici d'établir de façon simple l'équation de chacune des vagues, afin d'étudier les variations possibles du potentiel de demi-vague.

A. UNE SEULE DES DEUX FORMES EN ÉQUILIBRE EST RÉDUCTIBLE

Supposons que l'on trace la courbe de polarisation d'un oxydant Ox en équilibre avec un corps B *non réductible directement*, dans les conditions considérées.

Equation générale de la courbe de polarisation

Pour l'établir nous utiliserons une méthode déjà employée par l'un des auteurs de cet article[5].

Soient les deux réactions

$$\mathrm{B} \rightleftarrows \mathrm{Ox} \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$\mathrm{Ox} + n_T e \rightleftarrows \mathrm{Red} \quad \ldots\ldots\ldots\ldots \quad (2)$$

La réaction (1) est caractérisée par une constante d'équilibre K telle que

$$K = \frac{|\mathrm{Ox}|}{|\mathrm{B}|} \quad \ldots\ldots\ldots\ldots \quad (3)$$

La densité de courant *i* à une électrode donnée peut être calculée au moyen d'une équation de la forme

$$i = k\, n_T\, F |\mathrm{Red}|_{\mathrm{el}}\, \mathrm{e}^{\frac{\beta n F}{RT} E} - k'\, n_T\, F |\mathrm{Ox}|_{\mathrm{el}}\, \mathrm{e}^{-\frac{\alpha n' F}{RT} E} \quad \ldots\ldots\ldots \quad (4)$$

où E est le potentiel de cette électrode, k et k' des constantes caractéristiques du système Red/Ox envisagé, pour une électrode et une origine des potentiels données. n est le nombre d'électrons mis en jeu dans la réaction d'oxydation partielle la plus lente; n' a une signification analogue pour la réduction. $|\mathrm{Red}|_{\mathrm{el}}$ et $|\mathrm{Ox}|_{\mathrm{el}}$ sont les activités respectives du réducteur et de l'oxydant dans la couche de solution au contact de l'électrode.

Dans le cas envisagé, la vitesse de la réaction B $\rightleftharpoons$ Ox influe sur la concentration de l'oxydant à l'électrode. Pour calculer cette concentration nous supposerons qu'un état de régime est atteint et que par conséquent la variation des activités $|\mathrm{Red}|_{\mathrm{el}}$ et $|\mathrm{Ox}|_{\mathrm{el}}$ est nulle. Nous supposerons également que la migration de ces corps est nulle (grande concentration d'un électrolyte indifférent).

Considérons alors une électrode de 1 cm² de section. Dans la couche de solution en contact avec l'électrode, les bilans de chacun des corps sont donnés par[6]:

— Ox disparu par électrolyse + Ox amené par diffusion + Ox provenant de la dissociation de B = 0

Red apparu par électrolyse — Red enlevé par diffusion = 0

B amené par diffusion — B disparaissant par dissociation = 0.

En comptant positivement les courants anodiques et en représentant par X la quantité d'ions ou de molécules B qui se dissocient dans l'unité de temps les équations précédentes deviennent respectivement

$$\frac{i}{n_T F} + k_{d_1}' \left(|\mathrm{Ox}| - |\mathrm{Ox}|_{\mathrm{el}}\right) + X = 0 \quad \ldots\ldots\ldots \quad (5)$$

$$-\frac{i}{n_T F} + k_d \left(|\mathrm{Red}| - |\mathrm{Red}|_{\mathrm{el}}\right) = 0 \quad \ldots\ldots\ldots \quad (6)$$

$$k_{d_2}' \left(|\mathrm{B}| - |\mathrm{B}|_{\mathrm{el}}\right) - X = 0 \quad \ldots\ldots\ldots \quad (7)$$

$|\mathrm{Ox}|$, $|\mathrm{B}|$ et $|\mathrm{Red}|$ sont les activités au sein de la solution. k_{d_1}', k_{d_2}' et k_d sont les coefficients de diffusion habituels (ils font intervenir la constante de diffusion D et l'épaisseur de la couche de diffusion).

Dans la couche de solution en contact avec l'électrode nous admettrons que l'on peut encore écrire

$$X = k_R\, |\mathrm{B}|_{\mathrm{el}} - k_R'\, |\mathrm{Ox}|_{\mathrm{el}} \quad \ldots\ldots\ldots \quad (8)$$

$$\text{avec } K = \frac{k_R}{k_R'} \quad \ldots\ldots\ldots \quad (9)$$

Les coefficients k_R et k_R' ne sont pas les constantes de vitesse habituelles — qui se rapportent à une unité de volume — mais ils leur sont proportionnels.

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La résolution des équations (3) à (9) permet d'obtenir la relation générale

$$i = \frac{k\, n_T F|\mathrm{Red}|\mathrm{e}^{\frac{\beta nF}{RT}E} - k' n_T F|\mathrm{Ox}|\mathrm{e}^{-\frac{\alpha n'F}{RT}E}}{1 + \frac{k}{k_d}\mathrm{e}^{\frac{\beta nF}{RT}E} + \frac{k'\,(k_R + k_{d_2}')}{k_R k_{d_1}' + k_R' k_{d_2}' + k_{d_1}' k_{d_2}'}\mathrm{e}^{-\frac{\alpha n'F}{RT}E}} \quad \ldots\ldots \quad (10)$$

Cette équation est voisine de celle qu'ont récemment établie TAMAMUSHI ET TANAKA[10].

Lorsqu'aucune réaction chimique n'intervient, l'équation de la courbe de polarisation du système Red/Ox est[5]:

$$i = \frac{k\, n_T F|\mathrm{Red}|\,\mathrm{e}^{\frac{\beta nF}{RT}E} - k' n_T F|\mathrm{Ox}|\,\mathrm{e}^{-\frac{\alpha n'F}{RT}E}}{1 + \frac{k}{k_d}\mathrm{e}^{\frac{\beta nF}{RT}E} + \frac{k'}{k_d'}\mathrm{e}^{-\frac{\alpha n'F}{RT}E}} \quad \ldots\ldots\ldots\ldots\ldots \quad (11)$$

La comparaison des équations (10) et (11) montre que tout se passe comme si le coefficient de diffusion k_d' de Ox, dans le cas simple, était remplacé par

$$\frac{k_R\, k_{d_1}' + k_R'\, k_{d_2}' + k_{d_1}'\, k_{d_2}'}{k_R + k_{d_2}'} = \frac{K\, k_{d_1}' + k_{d_2}' + \frac{k_{d_1}'\, k_{d_2}'}{k_R'}}{K + \frac{k_{d_2}'}{k_R'}} \quad \ldots\ldots \quad (12)$$

Nous pouvons donc maintenant appliquer à l'équation (10) les résultats établis précédemment[5] pour l'équation (11).

Densité du courant limite

Les densités des courants limites anodique et cathodique sont respectivement

$$i_d = k_d\, n_T\, F|\mathrm{Red}| \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (13)$$

$$\text{et } i_l' = -\frac{K\, k_{d_1}' + k_{d_2}' + \frac{k_{d_1}'\, k_{d_2}'}{k_R'}}{K + \frac{k_{d_2}'}{k_R'}}\, n_T F|\mathrm{Ox}| \quad \ldots\ldots\ldots\ldots\ldots \quad (14)$$

$$\text{ou } i_l' = -\frac{K\, k_{d_1}' + k_{d_2}' + \frac{k_{d_1}'\, k_{d_2}'}{k_R'}}{K + \frac{k_{d_2}'}{k_R'}} \cdot \frac{K}{1 + K} \cdot n_T F\, c_T \quad \ldots\ldots\ldots \quad (15)$$

c_T étant la concentration totale $|\mathrm{Ox}| + |\mathrm{B}| = c_T$.

1) Si la réaction devient très lente $k_R' \to 0$

$$i_l' \to -\, k_{d_1}'\, n_T F|\mathrm{Ox}| = -\, k_{d_1}' \frac{K}{1 + K} n_T\, F c_T = i_d' ;$$

on obtient le courant limite de diffusion de l'oxydant Ox seul.

Ceci est réalisé dès que

$$\frac{k_{d_1}'}{k_R'} \gg 1 \text{ et } \frac{k_{d_2}'}{k_R'} \gg K \ldots\ldots\ldots\ldots \quad (16)$$

2) Si la réaction est très rapide $k_R' \rightarrow \infty$

$$i_l' \rightarrow -\left(k_{d_1}' + \frac{k_{d_2}'}{K}\right) n_T F|\mathrm{Ox}| = -n_T F(k_{d_1}'|\mathrm{Ox}| + k_{d_2}'|B|) = i_{dT}'.$$

La densité de courant limite est égale à la somme des courants limites de diffusion des corps B et Ox considérés séparément.

Cette équation est valable dès que

$$\frac{k_{d_1}'}{k_R'} \ll 1 \text{ et } \frac{k_{d_2}'}{k_R'} \ll \mathrm{K} \ldots\ldots\ldots\ldots \quad (17)$$

3) Si la réaction est complètement déplacée vers la formation de Ox, K est très grand

$$K \gg 1 \text{ et } K \gg \frac{k_{d_2}'}{k_R'} \ldots\ldots\ldots\ldots \quad (18)$$

$$\text{et} \quad i_l' = -k_{d_1}' n_T F c_T$$

$$i_l' \neq i_{dT}' \quad \text{si} \quad k_{d_1}' \neq k_{d_2}'.$$

Ceci est valable indépendamment des vitesses de réaction.

Des résultats analogues ont été établis par BRDICKA[34].

Nous utiliserons dans les applications une équation simplifiée obtenue à partir des précédentes en admettant $k_{d_1}' \neq k_{d_2}' = k_d'$

$$i_l' = \frac{K + 1 + \frac{k_d'}{k_R'}}{K + \frac{k_d'}{k_R'}} \cdot \frac{K}{1 + K} \cdot i_{dT}' \ldots\ldots\ldots\ldots \quad (19)$$

Variations du potentiel de demi-vague

1) Pour un système très réversible et dans la zone de réversibilité (c'est-à-dire dans une zone chevauchant l'intervalle défini par le potentiel normal d'équilibre et le potentiel d'équilibre dans les conditions expérimentales)[11], l'équation (11) peut être simplifiée et mise sous la forme

$$E = \frac{RT}{(\alpha n' + \beta n) F} \log \frac{k'}{\kappa} \frac{k_d\left(K + \frac{k_{d_2}'}{k_R'}\right)}{K k_{d_1}' + k_{d_2}' + \frac{k_{d_1}' k_{d_2}'}{k_R'}} + \frac{RT}{(\alpha n' + \beta n) F} \log \frac{i - i_l'}{i_d - i} \quad (20)$$

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La courbe a donc la forme classique puisque le terme variable est encore $\log \frac{i - i_l'}{i_d - i}$, mais le potentiel de demi-vague dépend des vitesses de réaction. En admettant encore $k_{d_1}' \neq k_{d_2}'$ on a

$$E_{1/2} = \frac{RT}{(\alpha n' + \beta n) F} \log \frac{k' k_d}{k k_d'} + \frac{RT}{(\alpha n' + \beta n) F} \log \frac{K + \frac{k_d'}{k_R'}}{1 + K + \frac{k_d'}{k_R'}} \quad . \; . \; . \quad (21)$$

$$= [E_{1/2}] + \frac{RT}{(\alpha n' + \beta n) F} \log \frac{K + \frac{k_d'}{k_R'}}{1 + K + \frac{k_d'}{k_R'}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (21')$$

$[E_{1/2}]$ étant le potentiel de demi-vague en l'absence de réaction chimique.

2) Dans la zone d'irréversibilité anodique, c'est-à-dire pour des potentiels suffisamment supérieurs au potentiel normal et au potentiel d'équilibre dans les conditions actuelles[11], l'équation (11) en première approximation peut être simplifiée:

$$E = \frac{RT}{\beta n F} \log \frac{k_d}{k} + \frac{RT}{\beta n F} \log \frac{i}{i_d - i} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (22)$$

comme en l'absence de réaction chimique.

Dans la zone d'irréversibilité cathodique, c'est-à-dire pour des potentiels suffisamment inférieurs au potentiel normal et au potentiel d'équilibre actuel, l'équation (11) devient:

$$E = \frac{RT}{\alpha n' F} \log \frac{k' \left(K + \frac{k_{d_2}'}{k_R'}\right)}{K\, k_{d_1}' + k_{d_2}' + \frac{k_{d_1}' k_{d_2}'}{k_R'}} + \frac{RT}{\alpha n' F} \log \frac{i_l' - i}{i} \quad . \; . \; . \; . \; . \; . \; . \quad (23)$$

Avec $k_{d_1}' \neq k_{d_2}' = k_d'$, le potentiel de demi-vague est:

$$E_{1/2}' = \frac{RT}{\alpha n' F} \log \frac{k'}{k_d'} + \frac{RT}{\alpha n' F} \log \frac{K + \frac{k_d'}{k_R'}}{1 + K + \frac{k_d'}{k_R'}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (24)$$

$$E_{1/2}' = [E_{1/2}'] + \frac{RT}{\alpha n' F} \log \frac{K + \frac{k_d'}{k_R'}}{1 + K + \frac{k_d'}{k_R'}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (24')$$

$[E_{1/2}']$ étant le potentiel de demi-vague cathodique en l'absence de réaction chimique.

Les équations (22), (23) et (24) s'appliquent au cas d'un système „irréversible" pour lequel i n'est mesurable que dans les zones d'irréversibilité. Dans ce cas les deux vagues ont des potentiels de demi-vague différents, et seul le potentiel de demi-vague cathodique est perturbé (dans le cas envisagé, où c'est l'oxydant qui participe à l'équilibre chimique).

L'écart $E_{1/2} - [E_{1/2}]$ pour un système très „réversible" ou l'écart $E_{1/2}' - [E_{1/2}']$ pour la vague cathodique d'un système oxydo-réducteur „irréversible", sont fonction de $\log \dfrac{K + \dfrac{k_d'}{k_R'}}{1 + K + \dfrac{k_d'}{k_R'}}$.

Comme nous l'avons fait pour la densité du courant limite de diffusion, nous pouvons prévoir les cas suivants:

a) Si la réaction est très lente $k_R' \to 0$, l'écart est nul, la vague est identique à celle obtenue avec la même concentration de Ox en l'absence de réaction chimique.

Ceci est réalisé dès que les conditions (16) sont vérifiées,

b) Si la réaction est très rapide $k_R' \to \infty$, (conditions (17)) l'écart observé est

$$E_{1/2} - [E_{1/2}] = \frac{RT}{(\alpha n' + \beta n)F} \log \frac{K}{1+K} \quad \ldots \ldots \ldots \ldots \quad (25)$$

$$\text{ou} \quad E_{1/2}' - [E_{1/2}'] = \frac{RT}{\alpha n' F} \log \frac{K}{1+K} \quad \ldots \ldots \ldots \ldots \quad (25')$$

c) Si la réaction est complètement déplacée vers la formation de Ox, K est très grand

$$E_{1/2} = [E_{1/2}] \quad \text{et} \quad E_{1/2}' = [E_{1/2}']$$

indépendamment de la vitesse de réaction.

La vague reste toujours identique à celle de Ox seul à la concentration c_T (conditions (18))

Le cas où le réducteur participe à une réaction chimique peut être traité de façon aussi simple.

B. LES DEUX CORPS EN ÉQUILIBRE SONT RÉDUCTIBLES

Equation de la courbe de polarisation

Pour simplifier les calculs nous envisageons seulement le cas particulier où les deux corps en équilibre sont réduits en donnant le même réducteur et où la réduction est réalisée irréversiblement.

Aux deux réactions

$$\mathrm{B} \rightleftarrows \mathrm{Ox} \quad \ldots \ldots \ldots \ldots \quad (1)$$

$$\mathrm{Ox} + n_T e \to \mathrm{Red} \quad \ldots \ldots \ldots \ldots \quad (2)$$

s'ajoute maintenant

$$\mathrm{B} + n_T e \to \mathrm{Red} \quad \ldots \ldots \ldots \ldots \quad (26)$$

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A un potentiel E donné Ox et B sont réduits en donnant respectivement des densités de courant

$$i_1 = - k_1' \, n_T \, F \, |\mathrm{Ox}|_{\mathrm{el}} \, \mathrm{e}^{-\frac{a_1 n_1' F}{RT} E} \quad \ldots\ldots\ldots\ldots\ldots \quad (27)$$

et

$$i_2 = - k_2' \, n_T \, F |\mathrm{B}|_{\mathrm{el}} \, \mathrm{e}^{-\frac{a_2 n'_2 F}{RT} E} \quad \ldots\ldots\ldots\ldots\ldots \quad (28)$$

d'après notre hypothèse de réduction irréversible. La densité de courant observée est

$$i = i_1 + i_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (29)$$

Dans les mêmes conditions que précédemment, le bilan de l'oxydant Ox est inchangé. Par conséquent l'équation (5) reste valable en remplaçant i par i_1:

$$\frac{i_1}{n_T F} + k_{d_1}'(|\mathrm{Ox}| - |\mathrm{Ox}|_{\mathrm{el}}) + X = 0 \quad \ldots\ldots\ldots\ldots\ldots \quad (5')$$

Le bilan de B est maintenant:

— B disparu par électrolyse + B amené par diffusion — B disparaissant par dissociation = 0.

et l'équation (6) est remplacée par

$$\frac{i_2}{n_T F} + k_{d_2}' \, (|\mathrm{B}| - |\mathrm{B}|_{\mathrm{el}}) - X = 0 \quad \ldots\ldots\ldots\ldots\ldots \quad (6')$$

Les équations (8) et (9) restent évidemment valables et la résolution de ce système d'équations permet de calculer

$$-\frac{n_T F \left[(k_1' |\mathrm{Ox}| \mathrm{e}^{-\frac{a_1 n_1' F}{RT} E} \left(1 + \frac{k_2'}{D} \cdot \frac{k_{d_1}'}{k_R'} \mathrm{e}^{-\frac{a_2 n_2' F}{RT} E} \right) + k_2' |\mathrm{B}| \mathrm{e}^{-\frac{a_2 n_2' F}{RT} E} \left(1 + \frac{k_1'}{D} , \frac{k_{d_2}'}{k_R'} \mathrm{e}^{-\frac{a_1 n_1' F}{RT} E} \right) \right.}{\left[1 + \frac{k_1' (K + \frac{k_{d'_2}}{k_R'})}{D} \mathrm{e}^{-\frac{a_1 n_1' F}{RT} E} \right] \left[1 + \frac{k_2' (1 + \frac{k_{d'_1}}{k_R'})}{D} \mathrm{e}^{-\frac{a_2 n_2' F}{RT} E} \right] - \frac{K \, k_1 k_2'}{D^2} \mathrm{e}^{-\frac{(a_1 n_1' + a_2 n_2') F}{RT} E}} \quad (30)$$

où $D = K k_{d_1}' + k_{d_2}' + k_{d_2}' \frac{k_{d_1}'}{k_R'}$

La relation (30) représente l'équation générale de la courbe de polarisation „irréversible" d'un mélange de deux corps réductibles en équilibre.

Discussion des différents cas possibles

1. Si la réaction est infiniment lente, pour une constante d'équilibre donnée, k_R' est négligeable et l'équation (30) peut être mise sous la forme

$$i = - \frac{k_1' n_T F |\mathrm{Ox}| \, \mathrm{e}^{-\frac{a_1 n_1' F}{RT} E}}{1 + \frac{k_1'}{k_{d_1}'} \mathrm{e}^{-\frac{a_1 n_1' F}{RT} E}} - \frac{k_2' n_T F \, |\mathrm{B}| \, \mathrm{e}^{-\frac{a_2 n_2' F}{RT} E}}{1 + \frac{k_2'}{k_{d_2}'} \mathrm{e}^{-\frac{a_2 n_2' F}{RT} E}} \quad \ldots\ldots \quad (31)$$

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La densité de courant (Fig. 1 courbe 1) est simplement la somme des densités de courant de deux composés indépendants (voir[5] page 181).

Si les constantes k_1' et k_2' sont suffisamment différentes, la courbe totale est formée de deux vagues successives de hauteur i_{d_1}' et i_{d_2}':

$$i_{d_1}' = -k_{d_1}' n_T F|\mathrm{Ox}| \quad (32) \quad \text{et} \quad i_{d_2}' = -k_{d_2}' n_T F|\mathrm{B}| \quad \ldots\ldots\ldots \quad (33)$$

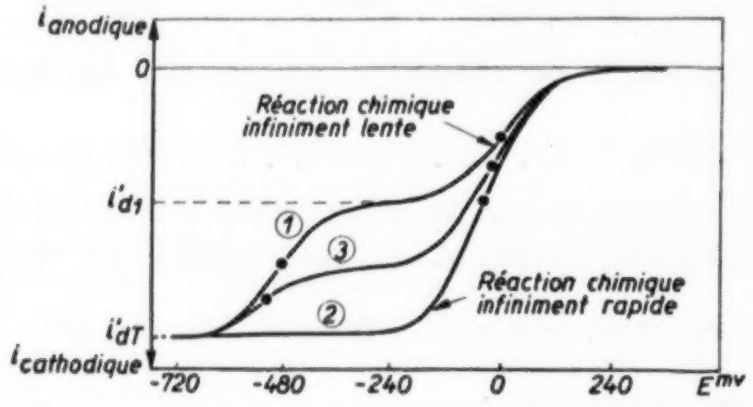

Fig. 1. Courbes calculées à partir de l'équation (30) en prenant $k_1' = k_{d_1}' = k_{d_2}' = K = |\mathrm{Ox}| = |\mathrm{B}| = 1$; $k_2' = 10^{-4}$; $a_n = \frac{1}{2}$; $k_R' = 0$ pour la courbe 1, $k_R' = 1$ pour la courbe 3, $k_R' = \infty$ pour la courbe 2.

la densité du courant limite total étant

$$i_{dT}' = -(k_{d_1}'|\mathrm{Ox}| + k_{d_2}'|\mathrm{B}|)\, n_T F \quad \ldots\ldots\ldots \quad (34)$$

Les potentiels de demi-vague sont

$$E'_{1/2,1} = \frac{RT}{a_1 n_1' F} \log \frac{k_1'}{k_{d_1}'} \quad \text{et} \quad E'_{1/2,2} = \frac{RT}{a_2 n_2' F} \log \frac{k_2'}{k_{d_2}'} \quad \ldots\ldots \quad (35)$$

Les deux vagues ont pour équations

$$E = E'_{1/2,1} + \frac{RT}{a_1 n_1' F} \log \frac{i_{d_1}' - i}{i} \qquad (0 < |i| < |i_{d_1}'|) \ldots\ldots \quad (36)$$

$$E = E'_{1/2,2} + \frac{RT}{a_2 n_2' F} \log \frac{i_{dT}' - i}{i - i_{d_1}'} \qquad (|i_{d_1}'| < |i| < i_{dT}') \ldots\ldots \quad (37)$$

2. Si la réaction est infiniment rapide, k_R' est infiniment grand et l'équation (30) devient

$$i = -\frac{n_T F\left(k_1'|\mathrm{Ox}|\mathrm{e}^{-\frac{a_1 n_1' F}{RT}E} + k_2'|\mathrm{B}|\mathrm{e}^{-\frac{a_2 n_2' F}{RT}E}\right)}{1 + \frac{k_1' K}{K k_{d_1}' + k_{d_2}'}\mathrm{e}^{-\frac{a_1 n_1' F}{RT}E} + \frac{k_2'}{K k_{d_1}' + k_{d_2}'}\mathrm{e}^{-\frac{a_2 n_2' F}{RT}E}} \quad \ldots\ldots \quad (38)$$

Lorsque le potentiel s'abaisse suffisamment pour que 1 soit négligeable par rapport aux autres termes du dénominateur on observe le courant limite dont la densité est

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$$i_{lT}' = -\frac{Kk_{d_1}'+k_{d_2}'}{1+K}\, n_T F(|\mathrm{Ox}|+|\mathrm{B}|) \quad \text{(39)}$$

avec $$i_{lT}' \neq i_{dT}' \text{ si } k_{d_1}' \neq k_{d_2}' \quad \text{(39')}$$

La courbe de polarisation ne présente qu'une seule vague.

Si Ox est beaucoup plus oxydant que B, $k_1' \gg k_2'$ et l'on peut écrire

$$i = -\frac{n_T F k_1' |\mathrm{Ox}|\, \mathrm{e}^{-\frac{a_1 n_1' F}{RT} E}}{1 + \frac{k_1' K}{Kk_{d_1}'+k_{d_2}'}\, \mathrm{e}^{-\frac{a_1 n_1' F}{RT} E}} \quad \text{(40)}$$

ou $$E = \frac{RT}{a_1 n_1' F} \log \frac{k_1' K}{Kk_{d_1}'+k_{d_2}'} + \frac{RT}{a_1 n_1' F} \log \frac{i_{lT}' - i}{i} \quad \text{(40')}$$

La densité de courant atteint la valeur limite i_{lT}' avant que le deuxième corps intervienne dans la réduction (Fig. 1 courbe 2).

Si $a_1 n_1' \neq a_2 n_2' = an'$, l'équation (38) devient

$$i = -\frac{n_T F(k_1' |\mathrm{Ox}| + k_2' |\mathrm{B}|)\, \mathrm{e}^{-\frac{an'F}{RT} E}}{1 + \frac{k_1' K + k_2'}{Kk_{d_1}'+k_{d_2}'}\, \mathrm{e}^{-\frac{1\,1}{RT} E}} \quad \text{(41)}$$

ou $$E = \frac{RT}{an'F} \log \frac{k_1' K + k_2'}{Kk_{d_1}'+k_{d_2}'} + \frac{RT}{an'F} \log \frac{i_{lT}' - i}{i} \quad \text{(41')}$$

Si aucune de ces deux dernières conditions n'est vérifiée, l'équation de la vague est plus compliquée.

3. Si les pouvoirs oxydants des deux corps Ox et B sont suffisamment différents, l'équation (30) peut être remplacée successivement par des formes plus simples pour les différentes valeurs de potentiel.

Supposons par exemple que $k_1' \gg k_2'$, on peut distinguer deux zones de potentiel.

a) Lorsque le potentiel est suffisamment élevé pour que les termes contenant $k_2'\, \mathrm{e}^{-\frac{a_2 n_2'}{RT} E}$ soient négligeables devant les autres termes de l'équation (30), celle-ci prend la forme

$$i = -\frac{n_T F k_1' |\mathrm{Ox}|\, \mathrm{e}^{-\frac{a_1 n_1' F}{RT} E}}{1 + \frac{k_1' K + \frac{k_{d_2}'}{k_R'}}{D}\, \mathrm{e}^{-\frac{a_1 n_1' F}{RT} E}} \quad \text{(42)}$$

qui est celle de l'équation (10) appliquée à un système „irréversible" (équation (23)) et discutée précédemment.

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Dans ces conditions la réduction de B est encore négligeable.

Le palier de la première vague est atteint lorsque

$$1 \ll \frac{k_1'K + \frac{k_{d_2}'}{k_R'}}{D}\, e^{-\frac{a_1n_1'F}{RT}E} \quad \ldots\ldots\ldots\ldots \quad (43)$$

Si cette condition est vérifiée en même temps que la précédente la courbe $i = \mathrm{f}(E)$ présente deux vagues nettement séparées.

b) Lorsque le potentiel est abaissé suffisamment, les termes contenant $k_2' e^{-\frac{a_2n_2'F}{RT}}$ cessent d'être négligeables. Par contre, l'inégalité (43) reste vérifiée. On peut alors mettre l'équation (30) sous la forme

$$i = -\frac{n_TF\left[|\mathrm{Ox}|D + k_2'\left(\frac{k_{d_2}'}{k_R'}|\mathrm{B}| + \frac{k_{d_1}'}{k_R'}|\mathrm{Ox}|\right)e^{-\frac{a_2n_2'F}{RT}E}\right]}{K + \frac{k_{d_2}'}{k_R'} + \frac{k_2'}{k_R'}e^{-\frac{a_2n_2'F}{RT}E}} \quad \ldots\ldots \quad (44)$$

ou encore sous la forme classique

$$E = E_{1/2}' + \frac{RT}{a_2n_2'F}\log\frac{i_{dT}' - i}{i - il_1'} \quad \ldots\ldots\ldots\ldots \quad (45)$$

avec

$$E_{1/2}' = \frac{RT}{a_2n_2'F}\log\frac{\frac{k_2'}{k_R'}}{K + \frac{k_{d_2}'}{k_R'}} \quad \ldots\ldots\ldots\ldots \quad (46)$$

$$i_{dT}' = -(k_{d_2}'\,|\mathrm{B}| + k_{d_1}'|\mathrm{Ox}|)n_TF \quad \ldots\ldots\ldots\ldots \quad (34)$$

et

$$il_1' = \frac{Kk_{d_1}' + k_{d_2}' + \frac{k_{d_1}'k_{d_2}'}{k_R'}}{K + \frac{k_{d_2}'}{k_R'}}\, n_TF|\mathrm{Ox}| \qquad \text{(voir équation (14))}$$

On obtient donc une vague d'allure normale, dont les densités de courant sont comprises entre la densité du courant limite de la première vague et celle du courant limite de diffusion de l'ensemble (Fig. 1 courbe 3).

C. APPLICATION AU CAS DES COMPLEXES ET DES ACIDES FOURNISSANT DEUX VAGUES CINÉTIQUES

Nous envisageons ici le cas d'une réduction irréversible. Le problème d'une oxydation irréversible peut être traité d'une façon analogue.

Deux cas sont à envisager selon que la première vague est due à la réduction de l'ion simple ou à celle du complexe ou de l'acide.

Equation de la première vague quand l'ion simple est réduit le premier

1. Le cas d'un complexe qui n'est pas susceptible d'être réduit aux potentiels considérés mais qui se dissocie avec une certaine vitesse en plusieurs particules dont l'une est réduite à l'électrode peut être ramené au cas simple précédent. Soit B le complexe qui se dissocie en deux particules dont l'une „Ox" est susceptible d'être réduite:

$$\mathrm{B} \underset{k_R'}{\overset{k_R}{\rightleftarrows}} \mathrm{Ox} + \mathrm{C}$$

Comme précédemment nous définissons les constantes K, k_R et k_R' par

$$\frac{|\mathrm{Ox}|}{|\mathrm{B}|} = \frac{K}{|\mathrm{C}|} \quad \text{et } X = k_R|\mathrm{B}|_{\mathrm{el}} - k_R'|\mathrm{C}||\mathrm{Ox}|_{\mathrm{el}}$$

Si l'on peut considérer que l'activité de C est la même à l'électrode et au sein de la solution, c'est-à-dire s'il y a un excès de C ou si la solution est tamponnée vis-à-vis de C, il suffit de remplacer K par $\frac{K}{|\mathrm{C}|}$ et k_R' par $k_R'|\mathrm{C}|$ pour être ramené au cas précédent.

Les équations (19), (23) et (24) deviennent:

$$E = E_{1/2,1}' + \frac{RT}{a_1 n_1' F} \log \frac{i_{l_1}' - i}{i} \quad \ldots\ldots\ldots\ldots \quad (47)$$

$$E_{1/2,1}' = \frac{RT}{a_1 n_1' F} \log \frac{k_1'}{k_d'} - \frac{RT}{a_1 n_1' F} \log \frac{K + |\mathrm{C}| + \frac{k_d'}{k_R'}}{K + \frac{k_d'}{k_R'}} \quad \ldots\ldots \quad (48)$$

$$i_{l_1}' = i_{dT}' \cdot \frac{K}{K + |\mathrm{C}|} \cdot \frac{K + |\mathrm{C}| + \frac{k_d'}{k_R'}}{K + \frac{k_d'}{k_R'}} \quad \ldots\ldots\ldots\ldots \quad (49)$$

2. En particulier $i_{l_1}' = i_{dT}'$ si $\frac{k_d'}{kR} \ll K$ et si $\frac{k_d'}{k_R'} \ll |\mathrm{C}|$ (conditions 17). La condition $\frac{k_d'}{k_R} \ll K$ dépend de la valeur des constantes de vitesse k_R et k_R'. Si la réaction B $\rightleftarrows$ Ox + C est suffisamment rapide cette condition est réalisée. La seconde condition dépend des conditions expérimentales dans lesquelles s'effectue l'électrolyse. Cette condition est réalisée quand la concentration de C devient élevée. Les équations (48) et (49) deviennent:

$$i_{l_1}' = i_{dT}' \quad \text{et } E_{1/2,1}' = \frac{RT}{a_1 n_1' F} \log \frac{k_1'}{k_d'} - \frac{RT}{a_1 n_1' F} \log \frac{K + |\mathrm{C}|}{K} \quad \ldots\ldots \quad (50)$$

et si $|\mathrm{C}|$ devient grand devant K:

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$$E^1/_{2,1}{}' = \frac{RT}{a_1 n_1' F} \log \frac{k_1'}{k_d'} + \frac{RT}{a_1 n_1' F} \log K - \frac{RT}{a_1 n_1' F} \log |\mathrm{C}| \quad \ldots\ldots \quad (51)$$

Cette équation est analogue à celle que LINGANE[6] et STACKELBERG et FREYHOLD[7] avaient établie dans le cas de la réduction réversible d'un complexe en équilibre rapide avec ses ions; mais nF est remplacé ici par $a_1 n_1' F$ et E_0 par $\frac{RT}{a_1 n_1' F} \log \frac{k_1'}{k_d'}$.

Cette équation est également valable si le complexe est un acide dont la base Ox est réduite avant l'acide et si l'équilibre entre l'acide, la base et les ions H$^+$ s'établit rapidement. Nous avons alors:

$$E^1/_{2,1}{}' = \frac{RT}{a_1 n_1' F} \log \frac{k_1'}{k_d'} - \frac{RT}{a_1 n_1' F} \mathrm{pK} + \frac{2.3 RT}{a_1 n_1' F} \mathrm{pH} \quad \ldots\ldots\ldots \quad (52)$$

Equation de la deuxième vague quand l'ion simple est réduit le premier

Comme précédemment il suffit de remplacer K par $\frac{K}{|\mathrm{C}|}$ et k_R' par $k_R' |\mathrm{C}|$ dans l'équation (46) de la deuxième vague. D'où

$$E = E^1/_{2,2}{}' + \frac{RT}{a_2 n_2' F} \log \frac{i_{dT}' - i}{i - i_{l_1}'} \quad (45) \qquad E^1/_{2,2}{}' = \frac{RT}{a_2 n_2' F} \log \frac{\frac{k_2'}{k_R'}}{K + \frac{k_d'}{k_R'}} \quad (53)$$

Le potentiel de demi-vague de la seconde vague est indépendant de $|\mathrm{C}|$, mais ce potentiel ne peut être décelé que si i_{l_1}' est différent de i_{d_T}' ce qui élimine d'après la discussion générale (page 474) les conditions $K \gg |\mathrm{C}|$ et $k_R' \to \infty$ qui entraineraient l'existence d'une seule vague.

Dans le cas particulier où $i_{l_1}' = i_{d_1}'$ (voir pages 473-474), c'est-à-dire si $\frac{k_d'}{k_R'} \gg K$ et $\frac{k_d'}{k_R'} \gg 1$ l'ion et le complexe se comporte comme deux éléments indépendants

$$E^1/_{2,2} = \frac{RT}{a_2 n_2' F} \log \frac{k_2'}{k_d'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (54)$$

Ce potentiel est indépendant de K que l'on ne peut espérer calculer à partir de l'écart entre les $E^1/_2$ des deux vagues.

Equation de la première vague quand le complexe (ou l'acide) est réduit le premier

1. Le cas d'un complexe qui est susceptible d'être réduit et de se dissocier avec une certaine vitesse en particules non électroactives peut également être ramené au cas simple Ox + ne → Red et B ⇄ Ox. Soit Ox le complexe qui se

dissocie en B et D non électroactifs aux potentiels considérés: $\mathrm{B} + \mathrm{D} \underset{k_R'}{\overset{k_R}{\rightleftarrows}} \mathrm{Ox}$

En conservant toujours les mêmes notations nous définissons les constantes K, k_R et k_R' par $\frac{|\mathrm{Ox}|}{|\mathrm{B}|} = \frac{|\mathrm{D}|}{K}$ et $X = k_R\,|\mathrm{D}|\,|\mathrm{B}| - k_R'\,|\mathrm{Ox}|$

Si l'on peut considérer que l'activité de D est la même à l'électrode et au sein de la solution, il suffit de remplacer K par $\frac{|\mathrm{D}|}{K}$ et k_R par $k_R\,|\mathrm{D}|$.

Les équations (19), (23) et (24) deviennent:

$$i_{l_1}' = i_{dT}' \frac{|\mathrm{D}|}{|\mathrm{D}|+K} \cdot \frac{|\mathrm{D}| + K + \frac{k_d'}{k_R}}{|\mathrm{D}| + \frac{k_d'}{k_R}} \quad \ldots\ldots\ldots\ldots\ldots \quad (55)$$

$$E_{1/2,1}' = \frac{RT}{a_1 n_1' F} \log \frac{k_1'}{k_d'} - \frac{RT}{a_1 n_1' F} \log \frac{|\mathrm{D}| + K + \frac{k_d'}{k_R}}{|\mathrm{D}| + \frac{k_d'}{k_T}} \quad \ldots\ldots\ldots \quad (56)$$

$$E = E_{1/2,1}' + \frac{RT}{a_1 n_1' F} \log \frac{i_{l_1}' - i}{i} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (47)$$

Le cas d'un acide réduit avant la base correspondante entre dans cette catégorie de réactions. Nous avons alors les équations suivantes:

$$i_{l_1}' = i_{dT}' \frac{|\mathrm{H}^+|\cdot}{|\mathrm{H}^+|+K} \frac{|\mathrm{H}^+| + K + \frac{k_d'}{k_R}}{|\mathrm{H}^+| + \frac{k_d'}{k_R}} \ldots\ldots\ldots\ldots\ldots \quad (57)$$

$$E_{1/2,1}' = \frac{RT}{a_2 n_1' F} \log \frac{k_1'}{k_d'} - \frac{RT}{a_1 n_1' F} \log \frac{|\mathrm{H}^+| + K + \frac{k_d'}{k_R}}{|\mathrm{H}^+| + k_R} \ldots\ldots\ldots \quad (58)$$

2. En particulier $i_{l_1}' = i_{dT}'$ si $\frac{k_d'}{k_R} \ll K$ (conditions 17) (c'est-à-dire si la réaction $\mathrm{B} + \mathrm{H}^+ \rightarrow \mathrm{Ox}$ est rapide) et si $\frac{k_d'}{k_R} \ll |\mathrm{H}^+|$ donc si le milieu est assez acide. Dans ce cas l'équation (58) devient

$$E_{1/2,1}' = \frac{RT}{a_1 n_1' F} \log \frac{k_1'}{k_d'}, - \frac{RT}{a_1 n_1' F} \log \frac{\mathrm{H}^+| + K}{|\mathrm{H}^+|} \quad \ldots\ldots\ldots\ldots \quad (59)$$

quand le pH est tel que $|\mathrm{H}^+| \gg \mathrm{K}$, nous avons

$$E_{1/2,1}' = \frac{RT}{a_1 n_1' F} \log \frac{k_1'}{k_d'} = \mathrm{C}^{\underline{\mathrm{te}}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (60)$$

Quand le pH est tel que $|\mathrm{H}^+| \ll K$

$$E_{1/2,1}' = \frac{RT}{a_1 n_1' F} \log \frac{k_1'}{k_d'}, + \frac{RT}{a_1 n_1 F} \mathrm{p}K - \frac{2.3\,RT}{a n' F} \mathrm{pH} \quad \ldots\ldots\ldots \quad (61)$$

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D'après les équations (52) et (61) nous voyons que $E_{1/2,1}'$ croît quand le pH augmente si la base est réduite avant l'acide, mais décroît quand le pH augmente si l'acide est réduit avant la base. Quand l'acide, la base et les ions H^+ sont en équilibre rapide, les courbes $E_{1/2,1}' = f(\text{pH})$ sont schématisées sur la Fig. 2.

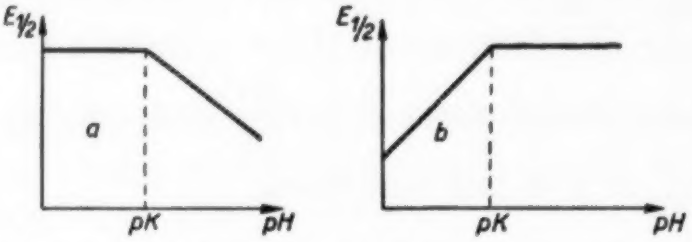

Fig. 2. (a) L'acide se décharge avant la base.
(b) La base se décharge avant l'acide.

Equation de la deuxième vague quand le complexe (ou l'acide) est réduit le premier

Comme précédemment il suffit de remplacer K par $\frac{|D|}{K}$ et k_R par $k_R|D|$ dans l'équation (46) de la seconde vague.

$$E = E_{1/2,2}' + \frac{RT}{a_2 n_2 F} \log \frac{i_{dT}' - i}{i - i_{l_1}'} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (45)$$

$$E_{1/2,2}' = \frac{RT}{a_2 n_2' F} \log \frac{\frac{k_2'}{k_R'}}{\frac{|D|}{K} + \frac{k_d'}{k_R'}} = \frac{RT}{a_2 n_2' F} \log \frac{\frac{k_2'}{k_R}}{|D| + \frac{k_d'}{k_R}} \quad \ldots\ldots \quad (62)$$

ou dans le cas d'un acide

$$E_{1/2,2}' = \frac{RT}{a_2 n_2' F} \log \frac{\frac{k_2'}{k_R}}{|H^+| + \frac{k_d'}{k_R}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (63)$$

D'après les équations précédentes nous voyons que $E_{1/2,2}'$ diminue quand $|D|$ ou $|H^+|$ augmente.

a) $|D| \gg \frac{k_d'}{k_R}$ ou $|H^+| \gg \frac{k_d'}{k_R}$

$$E_{1/2,2}' = \frac{RT}{a_2 n_1' F} \log \frac{k_2'}{k_R} - \frac{RT}{a_2 n_2' F} \log |D| \quad \ldots\ldots\ldots\ldots\ldots \quad (64)$$

D'après l'équation (55) $i_{l_1}' \neq i_{dT}'$ et dans ce cas $E_{1/2,2}'$ ne peut plus être décelé.

b) $|D| \neq \frac{k_d'}{k_R}$ $E_{1/2,2}'$ est donné par l'équation (62) et d'après l'équation (55) i_{l_1}' est différent de i_{dT}' dès que $|D| < K$

c) $|D| \ll \frac{k_d'}{k_R}$ ou $|H^+| \ll \frac{k_d'}{k_R}$

$$E_{1/2,2}' = \frac{RT}{a_2 n_2' F} \log \frac{k_2'}{k_d'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (65)$$

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$E_{1/2,2}'$ devient indépendant de $|\mathrm{D}|$ ou de $|\mathrm{H}^+|$. D'après l'équation (55) $i_{l_1}' \rightarrow 0$, on n'observe plus qu'une seule vague.

En résumé la valeur de $E_{1/2,2}'$ est constante dès que l'on n'observe plus qu'une seule vague, mais diminue si la première vague est présente. $E_{1/2,2}'$ ne varierait linéairement en fonction de log $|\mathrm{D}|$ ou du pH que dans le domaine où la densité de courant limite de la première vague masque complètement la deuxième.

Calcul des différentes constantes

Dans nos calculs nous avons fait intervenir les constantes k_d', k_1', k_2', k_R, k_R', et K, ces dernières étant reliées par $k_R = Kk_R'$.

La valeur de k_d' est connue et définie par $k_d' = \dfrac{i_{\text{diffusion}}}{|\mathrm{Ox}|}$, l'oxydant Ox étant seul présent dans la solution.

Les valeurs des constantes k_1', k_2', k_R' et K se déduisent de la façon suivante des équations définissant i_l' et $E_{1/2}$ (48) (49) (55) (56).

Les déformations de la première vague permettent de calculer k_1', k_R' et K, d'où k_R. En effet lorsque l'oxydant est seul présent dans la solution, la valeur de k_1' est déduite de l'équation

$E_{1/2}' = \dfrac{RT}{a_1 n_1' F} \log \dfrac{k_2'}{k_1'}$ le terme $\dfrac{RT}{a_1 n_1' F}$ étant déterminé par la pente de la droite $\log \dfrac{i_d' - i}{i} = \mathrm{f}(E)$.

Les valeurs de k_R' et de K sont déduites des équations (49) ou (55) et (48) ou (56).

$$i_{l_1}' = i_{dT}' \frac{K\left(K + |\mathrm{C}| + \dfrac{k_d'}{k_R'}\right)}{(K + |\mathrm{C}|)\left(K + \dfrac{k_d'}{k_R'}\right)} \text{ ou } i_{l_1}' = i_{dT}' \frac{|\mathrm{D}|\left(|\mathrm{D}| + K + \dfrac{k_d'}{k_R}\right)}{(|\mathrm{D}| + K)\left(|\mathrm{D} + \dfrac{k_d'}{k_R}\right)}$$

$$\triangle E_{1/2,1}' = \frac{RT}{a_1 n_1 F} \log \frac{K + |\mathrm{C}| + \dfrac{k_d'}{k_R'}}{K + \dfrac{k_d'}{k_R'}} \text{ ou } \triangle E_{1/2,2}' = \frac{RT}{a_1 n_1 F} \log \frac{|\mathrm{D}| + K + \dfrac{k_d'}{k_R}}{|\mathrm{D}| + \dfrac{k_d'}{k_R}}$$

Nous avons ici un système de deux équations à deux inconnues K et k_R', facile à résoudre.

La valeur du $E_{1/2}$ relatif à la deuxième vague permet de calculer k_2' d'après les équations

$$E_{1/2,2}' = \frac{RT}{a_2 n_2' F} \log \frac{\dfrac{k_2'}{k_R}}{|\mathrm{D}| + \dfrac{k_d'}{k_R}} \text{ ou } E_{1/2,2}' = \frac{RT}{a_2 n_2' F} \log \frac{\dfrac{k_2'}{k_R}}{|\mathrm{H}^+| + \dfrac{k_d'}{k_R}}$$

la constante K étant déterminée par ailleurs.

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Remarque: on ne peut jamais déduire la constante K de la valeur de $E_{1/2,2}'$ de la seconde vague dans le cas présent d'un échange d'électrons irréversible.

Application aux acides pyruvique et phénylglyoxylique

Etude de la première vague

Le système d'équations (57) et (58) permet d'interpréter les résultats expérimentaux de BRDICKA[8] relatifs à la réduction irréversible des acides pyruvique et phénylglyoxylique. L'auteur admet que l'acide est réduit le premier; on constate en effet que $E_{1/2,1}'$ décroît quand le pH augmente (voir page 484). Nous venons de montrer que l'on peut déduire la valeur des constantes k_R et K des équations $i = f(K, H^+, k_R)$ (57) et $E_{1/2,1}' = f(H^+, k_R, K)$ (58). Inversement si K est connu, en admettant l'exactitude de l'expression $i = f(K, H^+, k_R)$ on peut en déduire la courbe théorique $E_{1/2} = f(\mathrm{pH})$ et vérifier le bon accord de cette dernière et avec la courbe expérimentale.

L'expression de la densité de courant limite en fonction de l'activité des ions H^+ est analogue à celle que BRDICKA a établie et rend compte des résultats expérimentaux. En particulier $i_{l_1}' = \frac{1}{2} i_{dT}'$ quand $|H^+| = \frac{k_d'}{k_R}$ à condition que $|H^+| \ll K$.

BRDICKA trouve $i_{l_1}' = \frac{1}{2} i_{dT}'$ quand $|H^+| = 10^{-6.15}$ pour l'acide pyruvique et $H = 10^{-6.75}$ pour l'acide phénylglyoxylique. Comme les pK de ces deux acides sont respectivement 2.2 et 1.2, la condition $K \gg |H^+|$ est remplie. Nous avons donc $\frac{k_d'}{k_R} = 10^{-6.15}$ et $\frac{k_d'}{k_R} = 10^{-6.75}$ respectivement pour les acides pyruvique et phénylglyoxylique. Ces valeurs nous montrent que pour les deux acides K est très supérieur à $\frac{k_d'}{k_R}$.

Etude du potentiel de demi-vague

1. Dans le domaine de pH où $|H^+| \gg \frac{k_d'}{k_R}$ nous réalisons les conditions (64) donc $i_{l_1}' = i_{dT}'$. Dans ce domaine la réaction $B + H^+ \rightarrow Ox$ est rapide et $E_{1/2,1}'$ doit varier comme sur la figure (1a) d'après les équations (60) et (61).

2. Dans le domaine de pH où $|H^+| \neq \frac{k_d'}{k_R}$ les équations (57) et (58)

$$\text{donnent } i_{l_1}' = i_{dT}' \frac{|H^+|}{|H^+| + \frac{k_d'}{k_R}} \quad \ldots\ldots \quad (66)$$

$$\text{et } E_{1/2,1}' = \frac{RT}{\alpha_1 n' F} \log \frac{k_1'}{k_d'} - \frac{RT}{\alpha_1 n' F} \log \frac{K}{|H^+| + \frac{k_d'}{k_R}} \quad \ldots\ldots \quad (67)$$

3. Dans le domaine de pH où $|\mathrm{H}^+| \ll \frac{k_d'}{k_R}$ ces équations deviennent:

$$E_{1/2,1}' = \frac{RT}{\alpha_1' nF} \log \frac{k_1'}{k_d'} - \frac{RT}{\alpha_1 n' F} \log \frac{Kk_R}{k_d'} \quad \ldots\ldots\ldots\ldots\ldots \quad (68)$$

$$\text{ou } E_{1/2,1}' = \frac{RT}{\alpha_2 n' F} \log \frac{k_1'}{k_d'} - \frac{RT}{\alpha_1 n' F} \log \frac{k_R'}{k_d'} = (E_{1/2}')_{\text{final}} \quad \ldots\ldots \quad (68')$$

$i_{l_1}' \neq 0$

Dans ces conditions $E_{1/2,1}'$ ne devrait plus être décelable, mais il suffit que $i_{l_1}' = {}^1/_{10} i_{dT}'$ pour que $E_{1/2,1}' = (E_{1/2}')_{\text{final}}$ à moins de 5 mv près; il est alors encore possible de déterminer $E_{1/2}$ sur la courbe polarographique.

Autrement dit dans le cas des deux acides étudiés par BRDICKA, la courbe $E_{1/2,1}' = \mathrm{f(pH)}$ peut être divisée en trois parties:

1° En milieu très acide

$$E_{1/2,1}' = \frac{RT}{\alpha_1 n' F} \log \frac{k_1'}{k_d'} = (E_{1/2,1}')_{\text{initial}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (69)$$

la courbe est une droite parallèle à l'axe des pH.

2° En milieu peu acide

$$E_{1/2,1}' = \frac{RT}{\alpha_1 n' F} \log \frac{k_1'}{k_d'} + \frac{2.3RT}{\alpha_1 n_1 F} \mathrm{p}K - \frac{2\;3RT}{\alpha_1 n' F} \mathrm{pH} \quad \ldots\ldots\ldots \quad (70)$$

On obtient une droite de pente $-\frac{RT}{\alpha_1 n' F}$

3° En milieu alcalin

$$E_{1/2,1}' = \frac{RT}{\alpha_1 n' F} \log \frac{k_1'}{k_d'} - \frac{RT}{\alpha_1 n' F} \log \frac{k_R'}{k_d'} = (E_{1/2,1}')_{\text{final}} \quad \ldots\ldots\ldots \quad (68')$$

la courbe est une droite parallèle à des pH.

BRDICKA a exploré un domaine de pH compris entre 4 et 7.7 pour l'acide pyruvique et 2.2 et 9.24 pour l'acide phénylglyoxylique. Dans les deux cas l'auteur obtient une droite suivie d'un palier. Cette droite correspond à l'équation (70). La pente $-\frac{RT}{\alpha_1 n' F}$ permet de calculer $\alpha_1 n'$ et α_1 puisque $n = 2$ d'après MÜLLER $\alpha_1 = 0.33$ pour l'aide pyruvique $\alpha_1 = 0.30$ pour l'acide phénylglyoxylique. L'ordonnée à l'origine de la droite (70) et la connaissance du pK permet de calculer $\frac{RT}{\alpha_1 n' F} \log \frac{k_1'}{k_d'} = (E_{1/2,1}')_{\text{initial}}$.

On trouve $(E_{1/2,1}')_{\text{initial}} = -$ 905mv pour l'acide pyruvique
$(E_{1/2,1}')_{\text{initial}} = -$ 400mv pour l'acide phénylglyoxylique.

Connaissant la valeur du rapport $\frac{k_d'}{k_R}$ et le pK, l'équation (68) permet de calculer

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$(E_{1/2}')_{\text{final}}$ $(E_{1/2,1}')_{\text{final}} = -$ 1265 mv pour l'acide pyruvique
$(E_{1/2,1}')_{\text{final}} = -$ 980 mv pour l'acide phénylglyoxylique.

Il est donc possible de tracer la courbe théorique $E_{1/2,1}' = f(\text{pH})$. Nous reportons sur les Figures 3 et 4 les courbes théoriques et expérimentales et constatons que l'accord est satisfaisant.

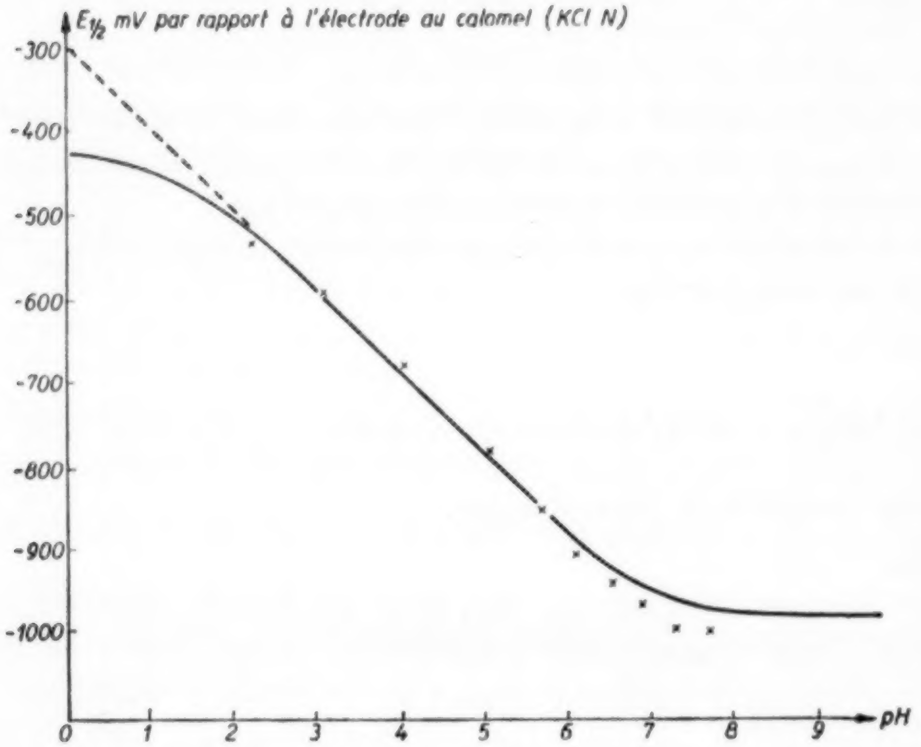

Fig. 3. Acide phénylglyoxylique
——— courbe théorique
× × × points expérimentaux

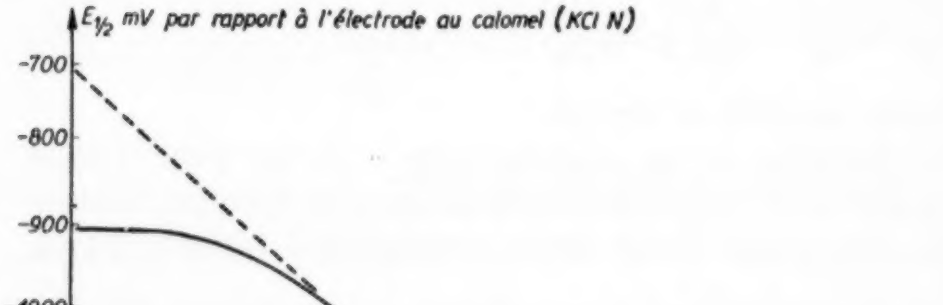

Fig. 4. Acide pyruvique
——— courbe théorique
× × × points expérimentaux

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Remarques: 1. Si la totalité de la courbe $E_{1/2,1}' = \mathrm{f}(\mathrm{pH})$ avait pu être déterminée expérimentalement il aurait été possible de calculer les pK des acides à partir des équations (69) et (70).

2. MÜLLER ET BAUMBERGER[9] ont également étudié les courbes polarographiques en fonction du pH; ils obtiennent en particulier un début de palier en milieu acide à partir de pH 1, mais dans l'ensemble leurs résultats diffèrent un peu de ceux de BRDICKA et vérifient moins bien les équations précédentes.

Etude de la seconde vague

On obtient bien pour les deux acides une valeur de $E_{1/2,2}'$ constante en présence d'une seule vague, soit —1580 mv pour l'acide pyruvique et —1265 mv pour l'acide phénylglyoxylique. Il n'est pas possible de déterminer la valeur de $E_{1/2,2}'$ pour l'acide pyruvique en présence des deux vagues car la réduction des ions H^+ se superpose partiellement à celle de l'anion. Par contre pour l'acide phénylglyoxylique le $(E_{1/2,2}')$ devient plus négatif en présence de la première vague comme le laisse prévoir l'équation (63) soit — 1290 mv à pH 6.

RÉSUMÉ

Nous avons établi les équations des vagues polarographiques observées lorsqu'une réaction chimique plus ou moins lente intervient avant l'échange d'électrons. La méthode de calcul est analogue à celle déjà utilisée par l'un des auteurs dans le cas des courbes de polarisation relatives à des systèmes ,,réversibles" ou ,,irréversibles".

Les variations des deux potentiels de demi-vague et des densités limites de courant en ont été déduites. Les résultats ont été vérifiés à partir des résultats expérimentaux de R. BRDICKA concernant les acides pyruviques et phénylglyoxylique.

SUMMARY

Equations have been established for polarographic waves observed while a chemical reaction slowly takes place before the exchange of electrons.

The method of calculation is analogous to that already used by one of the authors in the case of polarisation curves relative to the reversible or irreversible systems.

The variation of the two half-wave potentials and the limiting densities of current have been deduced. The results have been verified by means of the experimental results of R. BRDICKA concerning pyruvic and phenylglyoxylic acids.

ZUSAMMENFASSUNG

Wir haben die Gleichungen der polarographischen Stufen aufgestellt, die beobachtet werden, wenn von einem Elektronenaustausch eine mehr oder weniger langsame chemische Reaktion stattfindet. Die Methode der Ausrechnung ist analog einer, die schon von einem der Autoren im Fall relativer Polarisationskurven bei reversiblen oder irreversiblen Systemen benutz wurde.

Die Abhängigkeit der beiden Halbstufenpotential und der Grenzdichte des Stromes wurde abgeleitet. Die Ergebnisse wurden geprüft ausgehend von experimentellen Ergebnissen von R. BRDICKA bezüglich der Brenztraubensäure und der Phenylglyoxylsäure.

Bibliographie p. 490.

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Cambridge. 1952. (à paraître).

Reçu le 15 décembre 1952

SHORT COMMUNICATION

SEPARATION OF BERYLLIUM FROM ALUMINIUM AND IRON BY PAPER STRIP CHROMATOGRAPHY

by

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OSBORN AND JEWSBURY[1] carried out a separation of beryllium and aluminium by filter paper strip chromatography using a mixture of 80 per cent. of butanol and 20 percent. of AnalaR hydrochloric acid (v/v) and found the R_F values to be 0.3 and 0.03 respectively. This method takes as much as 18 hours.

In the present work the solution containing Fe, Al and Be as chlorides was applied to a strip of Whatman No. 1 filter paper 12" × 1½" and a mixture of 85 per cent. of methyl ethyl ketone and 15 per cent. of AnalaR concentrated hydrochloric acid (v/v) was used as a developing solvent employing the downward flow technique at a temperature of 70 deg. F. Table I gives the R_F values according to the notation suggested by LACOURT *et al.*[2].

TABLE I

Element	Amount µg	A/C	B/C
Al	240	0.12	0.26
Be	350	0.44	0.58
		Fe moves with the solvent front	

The above results show clearly that the tail of one element moves ahead of the front of the other indicating a clear separation.

Fluorescence technique[3] was used for identification of Al and Be after spraying with oxine.

Phosphate does not interfere with the separation but Ca and Mg do interfere since they move more or less with beryllium. Table II shows the relative amounts of the Be and Al that were tried and successfully separated by this technique.

References p. 492.

TABLE II

Aluminium μg	Beryllium μg
240	350
24	350
12	350
240	35
240	12

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[1] G. H. OSBORN AND A. JEWSBURY, *Nature*, 164 (1949) 443.
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Received March 30th, 1953

ANNOUNCEMENT

Arising from the success of the short Symposium on Analytical Chemistry held in Birmingham in 1952, it is proposed to run a larger Symposium from August 25th. to 1st. September 1954. This will consist of original papers and recent advances in various analytical fields.

An exhibition of new and special apparatus will be held simultaneously and visits to local places of interest will be organised.

A ladies committee has been formed to organise entertainment for non-scientific visitors.

Further details will be made available at a later date.

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NOUVELLE MÉTHODE D'ANALYSE QUALITATIVE DES ANIONS

par

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Cette étude constitue une tentative de mise au point concernant une méthode systématique d'analyse des anions dont l'idée première semble revenir à ENGELDER[1]. Cet auteur classait les anions d'après l'insolubilité des sels de calcium, baryum, zinc et argent.

Nous avons essayé d'introduire quelques améliorations visant à supprimer:

— l'existence de groupes mal équilibrés. Le premier groupe d'ENGELDER (sels de calcium insolubles) est en effet, beaucoup trop chargé;

— la caractérisation délicate d'anions présents dans un même groupe en raison de leurs réactions communes (arsénites et arséniates);

— la mise en solution problématique de sels très insolubles (chlorure, bromure, iodure d'argent);

— les procédés d'identification incertains.

Les modifications ont porté en général sur:

1°) *l'introduction du groupe supplémentaire* des sels de lithium insolubles, allégeant d'autant celui des sels de calcium.

2°) *la substitution du nitrate de plomb au nitrate d'argent* en vue de la séparation et de l'identification des anions du 4ème groupe d'ENGELDER.

Les avantages présentés par cette méthode paraissent être les suivants:

Les anions sont répartis en sept groupes équilibrés, réunissant des anions voisins par leurs propriétés générales (ex: chlorures, bromures, iodures, cyanures; ferrocyanures, ferricyanures, etc. . .). Inversement, les anions correspondant à des états d'oxydation différents d'un élément, prennent place dans des groupes différents, facilitant ainsi leur identification (arsénites et arséniates, hypophosphites et phosphates).

Les réactions sont nettes et spécifiques. Dans la mesure du possible, nous avons adjoint à une réaction principale et caractéristique, une réaction de contrôle aussi nette et spécifique que possible.

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[1] ENGELDER, *Elementary Qualitative Analysis,* John Wiley and Sons, New York.

Du point de vue pratique le mode opératoire retenu est rapide, les filtrations et le lavage des précipités s'opèrent sans difficulté; les séparations à l'intérieur des groupes sont immédiates. Suivant la technique moderne les séparations peuvent aussi bien s'effectuer par centrifugation.

Incompatibilités. Il n'est pas possible de donner un tableau complet des incompatibilités des anions; nombreuses, si la liqueur primitive ou la poudre ont un caractère acide, elles sont rares, en milieu neutre ou alcalin (exemples: silicate, fluorure, ou sulfure-ferricyanure.). C'est pourquoi nous avons écarté les traitements acides en cours d'analyse. L'appréciation des incompatibilités est laissée aux soins de l'analyste, à l'occasion de chaque cas particulier. Il convient de souligner trois causes fondamentales, responsables des incompatibilités:

— l'impossibilité de la présence simultanée des réducteurs et oxydants, surtout en milieu acide;

— l'insolubilité de certains sels; si la liqueur d'analyse est limpide avant tout traitement, la détermination des cations achevée, on pourra éliminer à priori la possibilité de présence de nombreux anions (chlorures, sulfates, sulfures, ferricyanures, etc. . . . insolubles);

— l'existence de complexes dont les propriétés diffèrent de celles des anions générateurs et qui ne permettent pas leur coexistence (exemple: fluosilicate) *.

Quelques essais préliminaires confirmeront ou infirmeront la présence de certains anions: appréciation du pH de la liqueur primitive; pouvoir d'oxydo-réduction.

La couleur de la liqueur sera notée (chromates, permanganates).

Dans le texte suivant nous avons parfois figuré une lettre entre parenthèses à la suite des réactions; nous rappelons ainsi l'ouvrage susceptible de fournir des indications sur le réactif signalé:

(D) Précis de Chimie Analytique. DENIGES-CHELLE-LABAT (E. Maloine 1930).

(D.G.) Analyse qualitative minérale. DELABY-GAUTHIER (Masson 1940).

(C) Théorie et méthode nouvelle d'analyse qualitative, CHARLOT (Masson 1949).

La méthode est fondée sur la séparation des anions en sept groupes.

Les anions du premier groupe sont caractérisés par un essai préliminaire **

Ils comprennent:

— les anions introduits par les réactifs de précipitation;

— les anions volatils susceptibles de disparaître en cours d'analyse;

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* Nous n'avons pas envisagé, d'une façon générale, les nombreux complexes dont l'anion renferme un métal.

** Parmi les sels d'une certaine importance, les chlorites, phosphites et periodates n'ont pas été classés.

Ces anions prendraient place normalement aux 2ème, 6ème et 7ème groupes.

Ier Groupe	CO_3^{-2}	(carbonates)
	NO_3^-	(nitrates)
	ClO^-	(hypochlorites)
	BrO^-	(hypobromites)
	$CH_3CO_2^-$	(acétates)

Si les essais contiennent des hypochlorites et des hypobromites, l'ébullition en présence de carbonate de sodium pourra entraîner la formation de chlorates et chlorures ou bromates et bromures.

Les anions des groupes suivants seront caractérisés sous forme de sels de sodium après traitement au carbonate de sodium *.

Ces anions se répartissent en cinq groupes séparés de façon systématique. Les liqueurs obtenues successivement sont précipitées par les nitrates de lithium, calcium, baryum, zinc et plomb.

2ème Groupe (sels de lithium insolubles)	fluorure	0.27 g/100 ml à 18°
	silicate	insoluble
	phosphate	0.039 g/100 ml à 18°
	arséniate	très peu soluble
	carbonate	1.33 g/100 ml à 20°

Il précipite partiellement du borate caractérisé au groupe suivant. Les carbonates ont été caractérisés au premier groupe.

3ème Groupe (sels de calcium insolubles)	oxalate	0.00067 g/100 ml à 13°
	iodate	0.13 g/100 ml à 0°
	molybdate	insoluble
	tungstate	insoluble
	arsénite	insoluble
	sulfite	0.0043 g/100 ml à 20°
	borate	0.2 g/100 ml à 10°

Il précipite partiellement du sulfate (0.23 g/100 ml à 20°) caractérisé au groupe suivant **.

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* Nous n'avons pas envisagé certains anions métalliques pouvant prendre naissance dans ces conditions. Ils auront été identifiés lors de la recherche des cations. Seuls les arsénites, arséniates, molybdates et tungstates ont été retenus car ils correspondent à l'état normal d'oxydation de l'élément envisagé. Les antimonites, antimoniates, stannites, stannates seraient précipités au troisième groupe où leur présence ne gêne pas la recherche des autres anions.

** On pourra rechercher le sulfate en agitant ce précipité avec de l'eau, acidulant la liqueur surnageante après séparation avec de l'acide chlorhydrique concentré et additionnant d'une goutte de solution de chlorure de baryum à 1%.

4ème Groupe (sels de baryum insolubles)	chromate	0.00034 g/100 ml à 16°
	fluosilicate	0.026 g/100 ml à 0°
	sulfate	0.00023 g/100 ml à 18°
	thiosulfate	très peu soluble
	bromate	0.8 g/100 ml à 15°
	ferrocyanure	0.17 g/100 ml à 15°

Les ferro cyanures sont également caractérisés au groupe suivant. Ce groupe peut contenir des traces d'iodate.

5ème Groupe (sels de zinc insolubles)	cyanure	0.005 g/100 ml à 20°
	ferrocyanure	insoluble
	ferricyanure	insoluble
	sulfure	insoluble

6ème Groupe (sels de plomb insolubles)	chlorure	0.99 g/100 ml à 20°
	bromure	0.84 g/100 ml à 20°
	iodure	0.063 g/100 ml à 20°
	thiocyanate	0.69 g/100 ml à 20°
	formiate	1.6 g/100 ml à 0°

Les hypochlorites et hypobromites détruits ou volatilisés par des ébullitions successives auront été détectés au cours des essais préliminaires.

Les anions non précipitables sous forme de sels de lithium, calcium, baryum, zinc et plomb, constituent le 7ème groupe:

7ème Groupe	permanganate
	hypophosphite
	nitrite
	chlorate
	formiate
	nitrate
	acétate

Les manganates seraient décelés par la coloration verte de la liqueur primitive virant au rouge violacé en milieu acide ou par dilution.

Les formiates ont été caractérisés au groupe précédent.

Les chlorures et bromures identifiés au 6ème Groupe, peuvent être recherchés d'une manière analogue.

Les nitrates et acétates ont été caractérisés au premier groupe.

ANIONS DU PREMIER GROUPE

CO_3^{-2}	(carbonates)
NO_3^-	(nitrates)
ClO^-	(hypochlorites)
BrO^-	(hypobromites)
$CH_3CO_2^-$	(acétates)

Les essais seront pratiqués sur la liqueur primitive ou sur la solution de la poudre à analyser dans l'eau tiède.

CO_3^{-2}: On le caractérise par dégagement d'anhydride carbonique: 1 ml de liquide est traité par quelques gouttes d'acide sulfurique dilué et de solution à 10% de chromate de potassium. Il se produit un dégagement gazeux. On adapte au tube à essai où se produit la réaction, un bouchon percé de deux trous, traversé par deux tubes de verre ouverts à leurs extrémités. L'un tiend a en suspension à l'intérieur du tube à essai une goutte d'eau de chaux qu'on animera d'un mouvement de va-et-vient en exerçant une suspression à l'aide du doigt obturant l'extrémité extérieure de l'autre. *L'eau de chaux se trouble*, les sulfites étant éventuellement détruits par le bichromate. On vérifiera que la goutte d'eau de chaux ne décolore pas une solution légèrement acide et très étendue de permanganate. Dans le cas de faibles quantités, il est recommandé de tiédir le mélange pour faciliter le dégagement. Avec de fortes proportions de carbonate, le carbonate de calcium préalablement formé peut se redissoudre. Les oxalates, difficilement réduits dans ces conditions, n'interfèrent pas.

NO_3^-: La recherche s'effectue par formation de dérivés nitreux du sulfate ferreux. Les nitrites sont tout d'abord détruits par l'urée ou mieux par l'acide sulfamique ou l'azoture de sodium, ces deux derniers réactifs n'étant pas susceptibles de les oxyder. A cet effet, la solution additionnée de quelques gouttes d'acide acétique et de quelques grains d'azoture de sodium est portée à l'ébullition.

A 1 ml de réactif (sulfate ferreux: 1 gramme dans 100 ml d'acide phosphorique à 80%), on superpose 5 gouttes de liquide pour essai. Un anneau *brun-rouge* se développe à la zone de contact et la coloration gagne la masse par agitation.

Contrôle: Formation de nitroantipyrine: à 10 gouttes de solution à essayer et 10 gouttes de solution à 5% d'antipyrine, on ajoute 1 ml d'acide sulfurique concentré. Il apparaît une *teinte rouge*. Il convient de superposer les liquides préalablement pour obtenir une réaction nette (D).

ClO^-: Le milieu sera caractérisé par un pouvoir oxydant élevé. Une mesure d'oxydo-réduction permettra d'en présumer l'existence (décoloration de sulfate d'indigo par exemple). Le réactif au plombite de sodium donnera à chaud un précipité *blanc, orangé,* puis *brun* (D).

La présence des hypochlorites sera démontrée par la mise en évidence de chlore dégagé en milieu acide (voir chlorures*). Les vapeurs coloreront en *bleu violet* un papier imbibé de réactif de VILLIERS ET FAYOLLE quand la liqueur acidulée par l'acide acétique sera portée à l'ébullition **.

BrO^-: Le milieu est également caractérisé par son pouvoir oxydant élevé. La présence des hypobromites sera démontrée par dégagement de brome en milieu acide (voir bromures). On acidule par l'acide acétique la liqueur à examiner dont les vapeurs colorent en *rose orangé* un papier imbibé de solution de fluorescéine, quand on la porte à l'ébullition. Toutefois dans ces deux derniers cas, si l'on trouve des bromates ou des chlorates coexistant avec des anions réducteurs au cours de l'analyse, il faudra envisager les possibilités d'interférence en milieu acide, avec dégagement de chlore et de brome en l'absence d'hypochlorites ou d'hypobromites.

$CH_3CO_2^-$: Formation d'oxyde de cacodyle; 5 ml de solution sont évaporés à sec; le résidu mélangé à son volume d'anhydride arsénieux est chauffé progressivement. Avant qu'il ne charbonne, on perçoit l'odeur repoussante de l'oxyde de cacodyle.

Contrôle: On additionne quelques gouttes de solution à examiner à 2 ml d'acide sulfurique. Il se dégage à chaud de l'acide acétique reconnaissable à son odeur. (La réaction est gênée par certains anions volatils.)

ANIONS DU DEUXIÈME GROUPE ET SUIVANTS

En vue des précipitations ultérieures, ces anions seront transformés en sels de sodium. Le traitement au carbonate de sodium sera pratiqué selon les indications suivantes:

— 100 ml de liqueur à analyser, ou 10 g de poudre délayée dans 100 ml d'eau sont additionnés de 20 g de carbonate de sodium. On porte 20 minutes à l'ébullition dans un ballon muni d'un réfrigérant ascendant ***. Après refroidissement le précipité de carbonates et d'oxydes métalliques est filtré et on vérifie que le filtrat ne précipite plus par une goutte de solution de carbonate de sodium.

Sur ce filtrat, on pratique la recherche des 2ème, 3ème, (etc. . . .) groupes.

ANIONS DU DEUXIÈME GROUPE

Précipitables par le nitrate de lithium.

On précipite la liqueur par la quantité nécessaire de solution de nitrate de lithium à l'ébullition. On filtre après refroidissement et vérifie que le filtrat ne précipite plus par une goutte de réactif. Il sera recueilli en vue de la recherche des anions du 3ème Groupe. Le précipité est lavé deux ou trois fois avec de l'eau froide.

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* Réaction donnée aussi par les chlorites qu'on pourra rechercher si la solution contient des chlorates, hypochlorites et chlorures.

** Prendre garde à la présence d'oxydants ou de mélanges générateurs de chlore ou de brome en milieu acide.

*** Dans le cas de résidus insolubles, on fera une fusion en présence de carbonate de sodium.

Il contient les anions:

F^-	(fluorure)
SiO_3^{-2}	(silicate)
PO_4^{-3}	(phosphate)
AsO_4^{-3}	(arséniate)
CO_3^{-2}	(carbonate)

La silice se combinant aux fluorures pour donner des fluosilicates, si on trouve des fluorures on ne recherchera pas les silicates, mais les fluosilicates au 4ème Groupe.

Inversement, si on identifie les silicates, on ne trouvera pas de fluorures. Le précipité est repris par l'acide chlorhydrique dilué et le mélange est filtré.

le précipité contient { fluorure

il passe en solution { silicate * phosphate arséniate

On recherche:

Dans le précipité: F^-: par formation de complexes fluorés de zirconium. Le complexe rouge zirconium-alizarine est décoloré en présence de fluorure. A 10 gouttes de liquide pour essai, on ajoute 3 gouttes d'acide chlorhydrique concentré puis le réactif (D.G.) goutte à goutte. La solution rouge violacée vire au *jaune.* Les phosphates et les arséniates ne gênent pas, étant éliminés par le traitement chlorhydrique et n'interférant qu'en fortes proportions.

Dans le filtrat: SiO_3^{-2}: formation de silice gélatineuse et de ses dérivés colorés.

5 gouttes de solution à examiner sont traitées par 2 ml d'acide sulfurique concentré et quelques grains de fluorure de sodium. On chauffe progressivement en exposant aux fumées blanches qui se dégagent, un agitateur portant 1 goutte d'eau: *un gel de silice* se forme sur la goutte d'eau par décomposition du fluorure de silicium formé. Cette réaction spécifique manque toutefois de netteté. Il convient de la rendre manifeste par formation d'acide silico-molybdique: l'agitateur est plongé dans une solution de soude à 5% chaude à laquelle on ajoute 2 gouttes d'une solution de molybdate d'ammonium à 5%, puis 2 ml d'acide sulfurique au 1/3. Il apparaît une *coloration jaune.* En déposant une goutte de cette solution sur un filtre sans cendres, avec une goutte de solution d'acétate de benzi-

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* La silice bien qu'insoluble dans l'eau, passe dans le filtrat à l'état colloïdal.

dine et quelques cristaux d'acétate de sodium, on fait apparaître une teinte *bleue* *.

PO_4^{-3}: formation de phosphomolybdate d'ammonium jaune insoluble.

A 1 goutte de liquide à essayer, on ajoute 1 ml de réactif phosphomolybdotartrique (obtenu en ajoutant 15 g d'acide tartrique à 100 ml de réactif nitromolybdique (C), et on porte à l'ébullition. Il se forme un *précipité jaune*. Après dépôt, la liqueur surnageante est incolore. Les arséniates et silicates n'interfèrent pas.

Contrôle. Formation de phosphate ammoniaco-magnésien.

A 1 goutte de solution de chlorure de magnésium à 5% on mélange une goutte de solution de chlorure d'ammonium à 5%, 2 gouttes de liquide à essayer, 1 ml d'ammoniaque et on agite. Il apparaît un *précipité blanc cristallin*. Les arséniates donnent la même réaction **.

AsO_4^{-3}: On précipite l'arsenic sous forme élémentaire par la méthode de BETTENDORF. A 2 gouttes de liquide à essayer, on ajoute 1 ml d'acide chlorhydrique concentré et 1 g de chlorure stanneux cristallisé, puis on porte à l'ébullition durant 1 minute. Il se forme un trouble brun, puis un *précipité gris-noir d'arsenic*.

Contrôle. Formation d'arsénimolybdate d'ammonium: Le réactif molybdique employé en excès donne un *précipité jaune*, à l'ébullition. La liqueur surnageante sera colorée en jaune clair.

ANIONS DU TROISIÈME GROUPE

Précipitables par le nitrate de calcium.

On précipite le filtrat du 2ème Groupe par la quantité nécessaire de nitrate de calcium à l'ébullition ***.

Le mélange est filtré après refroidissement et on vérifie que le filtrat ne précipite plus par une goutte de réactif. Il sera recueilli en vue de la recherche des anions du 4ème groupe.

Le précipité lavé plusieurs fois avec de l'eau froide, contient les anions:

$C_2O_4^{-2}$	(oxalate)
IO_3^{-}	(iodate)
MoO_4^{-2}	(molybdate)
WO_4^{-2}	(tungstate)
AsO_3^{-2}	(arsénite)
SO_3^{-2}	(sulfite)
BO_2^{-}	(borate)

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* Cette coloration bleue observée seule est sans signification car elle peut être provoquée par des traces d'autres éléments présents dans les réactifs. Un essai à blanc s'impose. Il faut considérer cette réaction comme apportant seulement une confirmation.

** Réaction parfois délicate à observer, le précipité étant peu visible et se formant lentement.

*** A froid, le molybdate ne précipite pas.

On reprend ce précipité par un grand excès d'acide acétique tiède à 20%.

le précipité non attaqué contient	oxalate iodate molybdate tungstate	il passe en solution	arsénite sulfite borate*

A) *le précipité* est traité par l'acide chlorhydrique 6*N*. Seuls les tungstates restent insolubles **. Dans la liqueur obtenue on caractérise:

$C_2O_4^{-2}$. Formation d'acide glyoxylique. Quoique seuls réducteurs du groupe, les oxalates sont difficiles à caractériser à ce point de vue. On emploiera la réaction spécifique suivante: 2 ml de la solution chlorhydrique sont traités par de la grenaille de zinc et 1 goutte de solution à 1% de sulfate de cuivre. On laisse agir l'hydrogène 5 à 10 minutes. Puis à 1 goutte du liquide obtenu diluée dans 1 ml d'eau on ajoute une parcelle de résorcinol et on porte à l'ébullition après avoir doublé le volume avec de l'acide chlorhydrique concentré. Il apparaît une *teinte jaune*. Par addition d'ammoniaque on obtient une *coloration rouge* et une *fluorescence verte*. Pendant la réduction, l'émission de vapeurs violettes décèle les iodates, et un *précipité bleu violet* le molybdène. Ces éléments ne gênent pas la caractérisation des oxalates.

Contrôle. Formation de bleu d'aniline: le liquide est évaporé à sec, dans une petite capsule. On ajoute quelques parcelles de diphénylamine et on chauffe encore avec précaution. Le résidu repris par l'alcool donne une *coloration bleue*.

IO_3^-. Formation d'iode. 1 ml de solution chlorhydrique est additionné de son volume d'eau et de quelques gouttes d'une solution de thiocyanate de potassium à 5%. Il y a coloration brune ***.

Contrôle. Cette coloration disparaît par addition de thiosulfate. Par agitation avec le benzène, l'iode colore le liquide en rouge, le chloroforme en violet.

MoO_4^{-2}. Formation de molybdo-thiocyanate. La solution précédente, après addition de thiocyanate de potassium (recherche des iodates) est traitée par quelques gouttes d'une solution concentrée de chlorure stanneux. Il apparaît une teinte *rouge violacée*, l'iode libéré, s'il y a des iodates, passant à l'état d'acide iodhydrique et ne gênant pas. Le colorant est soluble dans l'alcool benzylique.

Contrôle. Formation de complexes bleus du molybdène. A 1 ml de solution chlorhydrique pour essai, on ajoute 1 ou 2 gouttes de solution concentrée d'un phosphate alcalin et on porte à ébullition: il se forme un *précipité jaune*. 1 goutte de solution de chlorure stanneux dans le liquide obtenu donne une *coloration bleu*

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* Rechercher aussi les borates au groupe suivant, les sels de calcium et baryum précipitant souvent mal. Pratiquer l'essai également en liqueur primitive.

** Suffisamment pour que l'identification soit facile en tous cas.

*** Eviter la présence de fer dans les réactifs, qui donnerait une teinte rouge; sinon ajouter un peu de fluorure solide qui complexe le fer.

foncé; s'il y a des iodates il faut ajouter le chlorure stanneux goutte à goutte jusqu'à apparition de la teinte bleue.

Dans le précipité on caractérise:

WO_4^{-2}. Formation de composés inférieurs bleus. On ajoute au précipité une solution concentrée de chlorure stanneux chlorhydrique. Le précipité qui était jaune, devient bleu ou *vert noirâtre.* Un excès de chlorure stanneux ne modifie pas sa couleur. S'il était resté du molybdate, celui-ci solubilisé à l'état de sel trivalent donnerait une teinte brune. Par dilution, la confusion entre les deux anions n'est plus possible.

B) *Dans le filtrat:* On pratique la recherche des:

AsO_3^{-3}. Précipitation de l'arsenic élémentaire: A 2 gouttes de liquide à examiner, on ajoute 1 ml d'acide chlorhydrique concentré et 1 g de chlorure stanneux cristallisé. Il se forme, même à froid, un précipité brun noir. De petites quantités de molybdène passent parfois dans ce filtrat et donnent une *coloration brune.* Il suffit de diluer pour que la présence d'arsenic soit manifeste.

Contrôle. Formation de sulfure jaune: A la solution acétique diluée on ajoute une goutte de solution de sulfure de sodium. On observe un *précipité jaune.*

SO_3^{-2}. Dérivé coloré du nitrosoferricyanure: A 2 gouttes de la solution acétique, on ajoute quelques cristaux d'acétate de sodium puis 1 ml d'une solution à 1% de nitroprussiate de sodium et 1 ml de solution saturée de sulfate de zinc. Il apparaît une *coloration rose rouge* dont l'intensité augmente progressivement. Par addition d'une solution de ferrocyanure de potassium, il apparaît un *précipité rouge.*

Contrôle. Obtention du complexe cadmium-aniline: A 10 gouttes de liquide à essayer, on ajoute 10 gouttes d'eau et 3 gouttes de réactif au nitrate de cadmium-aniline de DENIGES (D). Il apparaît par agitation un léger *précipité cristallin blanc.*

BO_2^-. Transposition de curcumine en rosocyanine: On trempe un papier de curcuma jaune dans la solution acétique et on le sèche bien complètement: il se forme une *tache rose.* Cette tache au contact d'1 goutte de solution de soude normale prend une *couleur vert noirâtre* ou *vert brunâtre* (Comparer à la teinte rouge du papier alcalinisé). Dans ces conditions, la réaction est spécifique.

Contrôle. Complexe avec la quinalizarine: 1 goutte de solution à examiner et 2 ml d'une solution à 0.01 g de quinalizarine dans 100 ml d'acide sulfurique concentré donnent un virage du rose au *violet* en présence des borates. Il convient de faire un essai témoin.

ANIONS DU QUATRIÈME GROUPE

Précipitables par le nitrate de baryum.

On procède comme pour la précipitation précédente *.

Dans le filtrat on cherchera les anions du cinquième groupe.

Le précipité contient les anions:

CrO_4^{-2}	(chromate)
SiF_6^{-2}	(fluosilicate)
SO_4^{-2}	(sulfate)
$S_2O_3^{-2}$	(thiosulfate)
BrO_3^{-}	(bromate)
$[Fe(CN)_6]^{-4}$	(ferrocyanure)

On reprend ce précipité par l'eau bouillante, on filtre; par refroidissement les sels cristallisent.

Insolubles dans l'eau bouillante: chromate
fluosilicate
sulfate

Solubles dans l'eau bouillante: thiosulfate
bromate
ferrocyanure.

Dans le précipité du 1er sous-groupe on recherche:

CrO_4^{-2}. ** Formation d'un complexe rouge violacé avec la diphénylcarbazide; si la séparation d'avec les thiosulfates n'a pas été complète, les chromates dont la teinte jaune du précipité fait présumer l'existence, sont réduits en milieu acide. Il convient donc de porter à l'ébullition quelques instants, un peu de précipité dans 1 ml d'eau avec quelques grains de persulfate de potassium ***.

A 1 ml d'alcool on ajoute 2 ou 3 gouttes de solution de diphénylcarbazide et 1 ou 2 gouttes du liquide obtenu: il apparaît une *coloration violette* en présence d'acide chlorhydrique.

Contrôle: Formation d'acide perchromique bleu: la solution réoxydée, additionnée d'eau oxygénée et acidulée par quelques gouttes d'acide sulfurique est agitée aussitôt avec un peu d'éther. Après décantation, la couche éthérée est colorée *en bleu.*

$[SiF_6]^{-2}$ et SO_4^{-2}. Le précipité (1 gramme) est additionné de 4 grammes

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* Le ferrocyanure de baryum précipite mal à froid.

** La liqueur primitive possède une teinte jaune.

*** Un excès de persulfate détruirait la coloration donnée par la diphénylcarbazide.

de carbonate de sodium sec et de 5 à 10 ml d'eau, puis le mélange porté à l'ébullition durant 2 à 4 minutes. Le sulfate et le fluosilicate de baryum donnent une quantité suffisante de sels de sodium correspondants (le dernier sous forme de fluorure probablement), pour permettre une caractérisation directe dans la liqueur obtenue après filtration.

SiF_6^{-2}. On pratique l'essai alizarine-sulfonate de sodium zirconium, suivant les indications du paragraphe fluorure. Les fluosilicates donnent d'ailleurs la même réaction avec virage du rouge au *jaune* en milieu acide.

SO_4^{-2}. On le recherche sous forme de sel de baryum insoluble. A un mélange de 10 gouttes d'acide chlorhydrique $10N$, 2 ml d'eau, 3 gouttes de solution de chlorure de baryum à 10%, on ajoute 3 gouttes (jusqu'à 10 si la liqueur est peu concentrée) du filtrat précédent. Un *précipité blanc*, dense, de sulfate de baryum apparaît.

Contrôle. En milieu acide fort, sulfate et fluosilicate sont les deux seuls sels du groupe qui demeurent insolubles. En présence d'acide chlorhydrique ou nitrique, le précipité du 4ème groupe ne se solubilisera donc que partiellement.

Dans le précipité du deuxième sous-groupe on recherche:

$S_2O_3^{-2}$. Formation de sulfure d'argent noir. Le précipité est agité avec 1 ml d'eau additionné de quelques gouttes de solution de nitrate d'argent à 5%. Le précipité devient *jaune, orangé, brun* puis *gris noir* en une minute environ. Cette succession de couleurs est caractéristique.

Contrôle. L'essai précédent peut se pratiquer directement sur une parcelle du précipité prélevée immédiatement après précipitation par le nitrate de baryum.

BrO_3^-. Identification du brome. Le bromate pouvant être accompagné par de petites quantités d'iodate, on observera tout d'abord des vapeurs violettes, s'il y a de l'iode libéré. La réaction à la fluorescéine sera pratiquée suivant les indications du paragraphe: Bromure. La solution (1 ml) additionnée de quelques grains de sulfate ferreux et acidifiée par l'acide chlorhydrique libèrera par ébullition l'halogène, provoquant une tache *rose* d'éosine.

Contrôle. Formation d'un sel de manganèse trivalent: en l'absence de thiosulfates et de ferrocyanures on pourra tenter cette réaction spécifique. 2 gouttes de liquide à essayer, 1 ml de solution à 5% de sulfate manganeux sont acidulés par quelques gouttes d'acide sulfurique. Il se développe une *teinte rouge* dont l'intensité augmente progressivement; la liqueur portée à ébullition se trouble, il apparaît un précipité *brun.*

$[Fe(CN)_6]^{-4}$. Formation de bleu de Prusse: le précipité repris par 1 ml d'eau est additionné d'une goutte de solution de chlorure ferrique à 1%. Il apparaît un précipité *bleu foncé*. Cet essai peut être pratiqué directement sur le précipité des sels de baryum avant toute séparation.

Contrôle. Formation de ferrocyanure de cuivre: on ajoute à la liqueur une goutte de solution de sulfate de cuivre à 5%. Il se forme un précipité ***brun rouge.***

ANIONS DU CINQUIÈME GROUPE

Précipitables par le nitrate de zinc.

Les ferrocyanures s'ils sont présents en quantité notable, auront été caractérisés au groupe précédent. Sous forme de sels de zinc, ils sont difficilement identifiables. Il conviendra donc, avant traitement par le nitrate de zinc, d'ajouter au filtrat du groupe précédent un peu de chlorure ferrique en acidulant légèrement. S'il y a des ferrocyanures il se produit une coloration ou un précipité bleu.

Le filtrat est précipité à froid par une solution de nitrate de zinc.

On isole ainsi les anions:

CN^-	(cyanure)
$[Fe(CN)_6]^{-4}$	(ferrocyanure)
$[Fe(CN)_6]^{-3}$	(ferricyanure) *
S^{-2}	(sulfure) *

CN^-. Formation de bleu de Prusse: Le précipité est repris par une petite quantité d'acide chlorhydrique *N*. A l'ébullition, l'odeur d'amandes amères de l'acide cyanhydrique est perceptible. On présente à l'orifice du tube un papier trempé dans une solution de soude à 10%, sur lequel on dépose ensuite une goutte de solution de sulfate ferreux à 5%; le papier exposé aux vapeurs d'acide chlorhydrique se colore ***en bleu.***

Contrôle. Formation d'acide picrocyanique. A quelques parcelles de précipité, on ajoute un peu d'ammoniaque concentrée puis 1 ml de solution d'acide picrique à 1%. On porte à l'ébullition pendant 1 ou 2 minutes; il apparaît une couleur ***rouge orange*** ne disparaissant pas par l'acide chlorhydrique dilué. On pourra aussi caractériser les cyanures avant précipitation par le zinc au moyen de la décoloration des solutions colloïdales de sulfure de suivre (C).

$[Fe(CN)_6]^{-3}$. Couleur du sel de zinc et pouvoir oxydant: Le précipité de ferricyanure de zinc est jaune à jaune rougeâtre. On ajoute au précipité 1 ml d'eau et 1 ml d'acide acétique cristallisable. Le mélange agité avec quelques gouttes d'une solution acétique de diphénylamine à 1% donne une coloration ***vert mousse*** caractéristique. Agité avec 1 ou 2 gouttes de diéthylaniline, il donne une teinte ***brun jaune.***

S^{-2}. Formation de sulfure de plomb noir: On alcalinise le précipité franchement, par une solution de soude et on ajoute quelques gouttes de réactif au plombite de sodium (D). Il se forme un précipité ***noir*** caractéristique.

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* Ferricyanures et sulfures sont incompatibles.

Contrôle. Formation de sulfure de fer colloïdal. Le filtrat alcalinisé fortement par une solution de soude est additionné de quelques gouttes de soluté d'hydroxyde ferrique glycériné (D). Il apparaît une coloration *vert foncé.*

ANIONS DU SIXIÈME GROUPE

Précipitables par le nitrate de plomb.

Le filtrat précédent est traité à froid par la quantité nécessaire de solution de nitrate de plomb. On filtre convenablement le précipité ou on le lave avec très peu d'eau. Le filtrat est réservé à l'identification des anions du 7ème groupe.

Ce sixième groupe réunit les anions:

Cl^-	(chlorure)
Br^-	(bromure)
I^-	(iodure)
SCN^-	(thiocyanate)
HCO_2^-	(formiate)

On traite ce précipité par l'eau tiède et on filtre: *

Le précipité non dissous contient	iodure thiocyanate	sont solubilisés	chlorure bromure formiate

Dans le précipité on recherche:

I^-. Formation d'iode. On reprend un peu du précipité par 1 ml d'eau; on ajoute quelques grains de nitrite de sodium et acidule par l'acide nitrique. Le mélange agité en présence d'1 ml de benzène colore ce solvant en *violet rouge.*

Contrôle. Iodure de plomb; le précipité est repris par l'eau bouillante. On filtre. Par refroidissement il se forme des paillettes *dorées* d'iodure de plomb.

SCN^-. Formation de complexes pyridine-cuivre. Un peu de précipité repris par 1 ml d'eau auquel on ajoute 2 gouttes de pyridine et 1 goutte de solution de sulfate de cuivre à 0.5% se transforme en un précipité *vert* caractéristique.

Contrôle. Formation de sulfocyanure ferrique: une parcelle de précipité reprise par 1 ml d'eau est agitée après addition d'1 goutte de solution de chlorure ferrique à 0.05%. Il se produit une coloration *rouge* disparaissant par addition d'un fluorure solide à la solution.

Dans le filtrat on recherche:

Cl^-. Dérivés d'oxydation de l'orthotoluidine. On traite 0.5 ml de filtrat par 1 ml d'acide sulfurique concentré et quelques grains de bioxyde de manganèse. Le liquide est porté avec précaution à l'ébullition dans un tube à essai, dont

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* L'eau bouillante solubiliserait l'iodure notablement, ce qui pourrait gêner la recherche du chlore et du brome.

l'orifice sera obturé par un papier filtre imbibé au moment de l'emploi de réactif de VILLIERS ET FAYOLLE.

Une tache *bleu violacée* indique la présence du chlore. On fera un essai à blanc pour s'assurer de la pureté des oxydes de manganèse employés.

Br^-. Formation d'éosine: le mode opératoire est identique à celui pratiqué dans le cas des chlorures. On présente à l'orifice du tube un papier imbibé de solution de fluorescéine. Il se forme une tache *rose* plus visible après dessiccation.

SCN^-. Les thiocyanates sont présents également dans le filtrat; on les caractérisera par les deux essais décrits dans le cas du précipité.

HCO_2^-. Formation de formiate d'éthyle: quelques gouttes de solution sont chauffées avec un peu d'alcool éthylique et 1 ml d'acide sulfurique concentré. On perçoit une odeur de rhum caractéristique.

Contrôle. Formation de formiate basique: à 1 ml du filtrat neutre, on ajoute 1 ou 2 gouttes de solution de chlorure ferrique à 5%. Il apparaît une coloration *rouge*, mais la réaction est masquée si les thiocyanates sont présents. Par ébullition, on obtient un précipité de couleur *rouille*.

ANIONS DU SEPTIÈME GROUPE

Ce sont les anions suivants auxquels se joignent ceux du 6ème groupe dont les sels de plomb sont sensiblement solubles (chlorure, bromure, formiate). On pourra les caractériser comme précédemment.

MnO_4^-	(permanganate)
$H_2PO_2^-$	(hypophosphite)
NO_2^-	(nitrite)
ClO_3^-	(chlorate)
$CH_3CO_2^-$	(acétate)
NO_3^-	(nitrate)

Acétate et nitrate introduits en cours d'analyse ont été déterminés au premier groupe.

Dans la liqueur on recherche directement:

MnO_4^-. Couleur: ce sont les seuls sels colorés du groupe. La liqueur présente une couleur rouge violacée disparaissant en présence d'un réducteur en milieu acide. A une goutte de liqueur on ajoute 1 ml de lessive de soude très concentrée: la couleur vire au *vert*. Si la solution primitive était très alcaline et de teinte verte elle serait susceptible de renfermer des manganates. Elle virerait alors, au rouge par acidification, ou même, par simple dilution. En milieu neutre, la réduction du permanganate est encore possible mais il apparaît un précipité de bioxyde de manganèse. Au contact du papier filtre cette réaction se produit déjà sensiblement.

$H_2PO_2^-$. Formation de phosphate: On fait bouillir 2 gouttes de liqueur avec 1 ml d'eau et 1 ml d'acide nitrique, puis on précipite par le réactif molybdique (voir phosphate).

Contrôle. En milieu acide le liquide manifeste un fort pouvoir réducteur.

Il précipite du cuivre ou de l'argent par réduction des solutions de leurs sels.

NO_2^-. Formation de colorants azoïques. A 1 ml d'une solution de 0.5 g d'acide sulfanilique dans l'acide acétique à 30%, on ajoute 1 goutte de solution à essayer très diluée, puis quelques gouttes d'une solution acétique à 1% de naphtylamine α. Il apparaît une teinte *rose*.

On peut aussi pratiquer la réaction de ZAMBELLI (Le réactif est préparé en dissolvant 2 g d'acide sulfanilique et 3 g de phénol dans 200 ml d'acide chlorhydrique 3*N*, tiédissant pour dissoudre et ajoutant après refroidissement 60 g de chlorure d'ammonium dissous dans 200 ml d'eau.) A 1 ml de réactif on ajoute 1 goutte de liquide pour essai, laisse agir dix minutes puis neutralise par l'ammoniaque: il apparaît une teinte *jaune*. Les nitrates ne gênent pas.

Contrôle. Réaction de DENIGES: on chauffe à 60° quelques instants 2 gouttes de liquide pour essai avec 1 ml de réactif acétophénolmercurique de DENIGES (D). Une teinte *rouge* se développe. La réaction est spécifique.

ClO_3^-. Formation de dérivés d'oxydation colorés de l'aniline: après avoir détruit les nitrites, on agite 1 goutte d'aniline avec 1 ml d'eau, puis on ajoute 2 à 3 gouttes de solution à examiner et enfin, 1 à 2 ml d'acide sulfurique concentré. Il apparaît une coloration *bleue*. Les nitrates ne donnent pas cette réaction.

Les perchlorates pourraient être recherchés après action de l'hydrosulfite qui les transforme en chlorures, après élimination des chlorates par l'anhydride sulfureux, et des chlorures formés ou présents au moyen d'un sel d'argent. Ils précipitent de plus en *bleu violet* les solutions diluées de bleu de méthylène.

Contrôle. Transformation en chlorure: On précipite 5 ml de la liqueur du 7ème groupe par la quantité nécessaire de solution de nitrate d'argent sans excès. Le filtrat ne doit plus précipiter. Il est additionné de son volume d'acide acétique concentré et de poudre de zinc. Le liquide est porté à l'ébullition pour faciliter la réduction puis on dilue pour éviter la précipitation de nitrite d'argent. On ajoute quelques gouttes de solution de nitrate d'argent à 5%. Il apparaît un précipité *blanc* de chlorure d'argent.

RÉSUMÉ

Ce travail concerne une méthode systématique d'analyse des anions. Elle repose sur la séparation des anions en 7 groupes, fondée sur l'insolubilité des sels de lithium, calcium, baryum, zinc et plomb. Dans chaque groupe se trouvent décrites une réaction d'identification spécifique et une réaction de contrôle pour chaque anion.

SUMMARY

This work deals with a systematic method of analysing anions. It relies on the separation of the anions into 7 groups, based on the insolubility of the salts of

lithium, calcium, barium, zinc and lead. In each group a specific identification reaction is described and a control reaction for each anion.

ZUSAMMENFASSUNG

Diese Arbeit handelt über eine systematische Anionenanalysenmethode. Sie beruht auf der Trennung der Anionen in 7 Gruppen, die sich auf die Unlöslichkeit der Lithium-, Calcium-, Barium-, Zink- und Bleisalze stützt. In jeder Gruppe wird eine spezifische Identifikationsreaktion und eine Kontrollreaktion für jedes Anion beschrieben.

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DOSAGE DU SILICIUM PAR PRÉCIPITATION DU COMPLEXE SILICOMOLYBDIQUE JAUNE PAR LA QUINOLÉINE

par

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INTRODUCTION

Les méthodes colorimétriques de dosage du silicium, basées sur la mesure de l'absorption de la lumière par le complexe silicomolybdique jaune ou par ses produits de réduction bleus, permettent d'envisager le dosage précis de cet élément jusqu'à des concentrations de l'ordre de 0.1 mg par litre. Malheureusement, comme il s'agit en fait de méthodes relatives, elles nécessitent un étalonnage qui doit être effectué par une méthode absolue. Or, les méthodes absolues classiques reposant sur l'insolubilisation de la silice en milieu acide sont pratiquement inapplicables pour des concentrations aussi basses, en raison de l'importance des prises d'essais qu'elles nécessitent.

A la suite de notre travail sur la formation du complexe silicomolybdique[1] nous avons été tout naturellement amenés à étudier sa précipitation par certaines bases organiques. Cette précipitation, proposée ces dernières années par divers auteurs[2 à 8], semble en effet fournir une solution élégante aux difficultés mentionnées ci-dessus, en raison de l'importance des facteurs analytiques mis en jeu. Parmi les nombreuses bases utilisables, nous avons choisi la quinoléine parce qu'elle permet en outre un dosage volumétrique simple.

RAPPEL DES PROPRIÉTÉS OPTIQUES ET DES CONDITIONS DE DÉVELOPPEMENT DU COMPLEXE-JAUNE

Propriétés optiques

En lumière monochromatique, la coloration des solutions d'acide silicomolybdique suit rigoureusement la loi de LAMBERT-BEER; le coefficient d'absorption croît lorsque la longueur d'onde diminue de 5,600 à 3,600 A, mais il dépend en outre, comme nous le verrons par la suite, du pH de formation et du temps.

Bibliographie p. 525.

Conditions de développement

On admet en général que le complexe se forme suivant la réaction:

$$SiO_3^{-2} + 12\ MoO_4^{-2} + 22\ H^+ \rightleftarrows Si(Mo_3O_{10})_4^{-4} + 11\ H_2O$$

Les principaux facteurs de cet équilibre sont:

— la concentration en silicium
— la concentration en molybdate
— l'acidité
— la température

Concentration en silicium

La réaction n'est possible qu'à partir d'acide silicique en solution vraie, et ces solutions ne sont stables un certain temps qu'au-dessous de 100 mg de silicium par litre.

Concentration en molybdate

Pour une concentration en silicium donnée, un certain excès de molybdate est nécessaire pour obtenir le développement total du complexe. Cet excès est d'environ 2.5 g de paramolybdate d'ammonium par litre, à pH 1.0.

Acidité

La zone de pH dans laquelle la réaction est complète et rapide dépend de la concentration en paramolybdate d'ammonium C: elle augmente notablement avec celle-ci ($1.5 < \text{pH} < 3.5$ pour $C = 1$ g $^0/_{00}$; $0.7 < \text{pH} < 4.5$ pour $C = 10$ g $^0/_{00}$). Au-dessous de cette zone, la réaction devient plus lente et sa vitesse dépend en outre de la nature de l'acide utilisé. Le coefficient d'absorption monochromatique du complexe croît légèrement lorsque le pH de développement diminue. Aux bas pH cependant, il évolue lentement dans le temps (24 heures environ) pour tendre vers la valeur correspondant aux pH élevés.

Température

Une élévation de la température accélère tous les phénomènes précédents. Le complexe peut se développer en milieu plus acide et, à 80° par exemple, son évolution complète ne demande plus qu'une heure environ.

Ces divers phénomènes s'expliquent assez bien par la loi d'action de masse et pour plus amples détails, nous renvoyons à notre premier mémoire.

Deux points cependant restaient obscurs:

— la variation du coefficient d'absorption en fonction du pH et du temps
— l'influence de la nature de l'acide sur la vitesse de développement du complexe.

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Depuis la publication de nos résultats, nous avons eu connaissance d'un certain nombre de travaux qui viennent les confirmer et les éclairer d'un jour nouveau.

En se basant sur les caractères des produits de réduction par $SnCl_2$, STRICKLAND[9] a établi l'existence de deux formes isomères du complexe, α et β, présentant, en solution, des spectres d'absorption voisins, mais des coefficients d'absorption différents. Le développement de l'une ou l'autre de ces formes dépend de la valeur du rapport $R = \frac{\text{concentration en } H^+}{\text{concentration en } MoO_4^{-2}}$ (concentrations exprimées en équivalents). La forme α apparaît seule pour $1.5 < R < 2.0$. Pour $2 < R < 3$, on obtient un mélange de α et β. Au-delà, β est le seul constituant initial, mais il se transforme lentement et de façon irréversible en α.

FERRARI[10] a également observé des variations lentes de l'absorption du complexe, qu'il attribue à l'existence d'une forme colorée et d'une forme incolore se formant successivement. Mais son interprétation ne tient pas devant celle de STRICKLAND. Par contre, nous considérons comme très plausible son explication du ralentissement de la réaction aux fortes acidités par la formation de complexes molybdiques à partir de l'anion de l'acide, car elle permet de rendre compte de l'influence de la nature de l'acide. Nous pensons cependant que les ions H^+ doivent eux aussi être rangés parmi les ions complexant.

ÉTUDE EXPÉRIMENTALE DE LA PRÉCIPITATION

D'après WILSON, la précipitation du complexe silicomolybdique par la quinoléine a lieu suivant la réaction:

$$4\,[C_9H_7N)\,HCl] + H_4SiO_4.12\,MoO_3 \rightleftarrows (C_9H_7N)_4\,H_4SiO_4\,.\,12\,MoO_3 + 4\,HCl$$

Dans son article, cet auteur n'envisage qu'un dosage volumétrique basé sur la dissolution du précipité dans la soude titrée, suivie d'un dosage alcalimétrique en retour.

Nous nous sommes au contraire attachés à examiner les possibilités d'un dosage gravimétrique et, dans ce but, nous avons cherché à préciser les propriétés du précipité et ses conditions de formation.

Etude du précipité et de ses propriétés

Les essais de précipitation par la quinoléine confirment entièrement l'hypothèse de STRICKLAND relative à l'existence de deux formes isomères du complexe. Les précipités obtenus à partir de chacune des deux formes sont en effet nettement différents, tant par leur aspect que par leurs propriétés.

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Le complexe *α*, qu'il soit le résultat d'un développement direct en milieu peu acide, ou le terme final de l'évolution du complexe *β* à froid ou à chaud, forme un précipité jaune pâle, décantant assez rapidement, mais difficile à filtrer sur verre fritté, même après un chauffage prolongé à 80°, car il colmate rapidement les filtres (voir mode de préparation annexe Ia).

Le complexe *β* donne un précipité d'un jaune beaucoup plus franc, décantant également très bien et se filtrant facilement après un chauffage de courte durée à 80° (voir mode de préparation annexe Ib).

Examen des précipités

Les précipités décrits ci-dessus ont été soumis à une étude thermogravimétrique à la balance de CHEVENARD et à des examens aux rayons X.

Etude à la thermobalance

Les courbes de perte de poids des deux types de précipités sont pratiquement identiques; on y observe successivement:

— le séchage entre 26° et 110°

— le départ de deux molécules d'eau et quatre molécules de quinoléine entre 250° et 480°

— la volatilisation de MoO_3 entre 780° et 1,000° (voir Fig. 1).

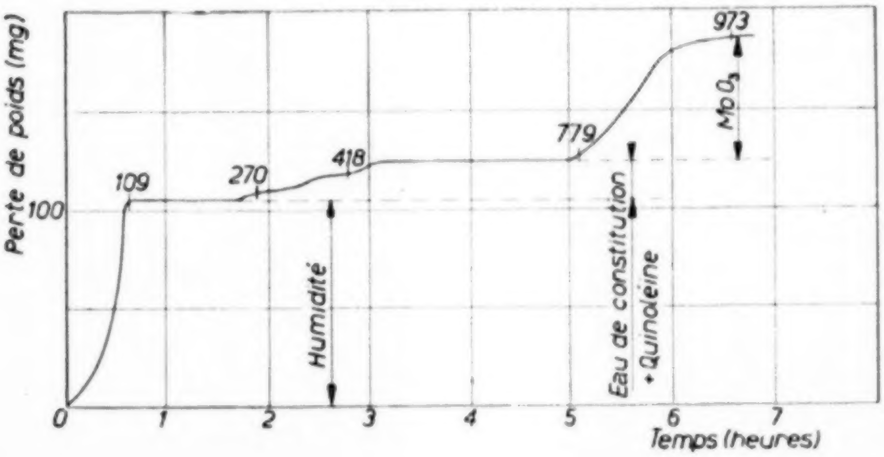

Fig. 1. Analyse thermogravimétrique du précipité *β* humide.
Perte de poids en fonction du temps pour une vitesse de chauffage de 150°/heure.

Les phénomènes sont encore plus nets dans le cas des précipités préalablement débarrassés de la plus grande partie de leur humidité. Le dépouillement quantitatif des courbes correspondantes permet d'établir les compositions suivantes pour les produits secs:

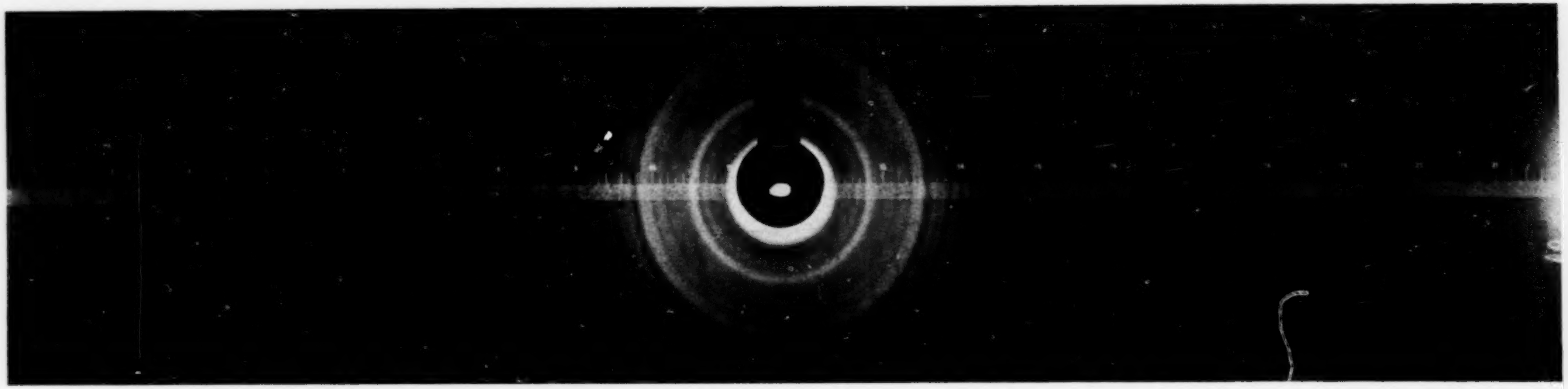

Fig. 2. Diagramme de diffraction aux rayons X du précipité *α* séché.

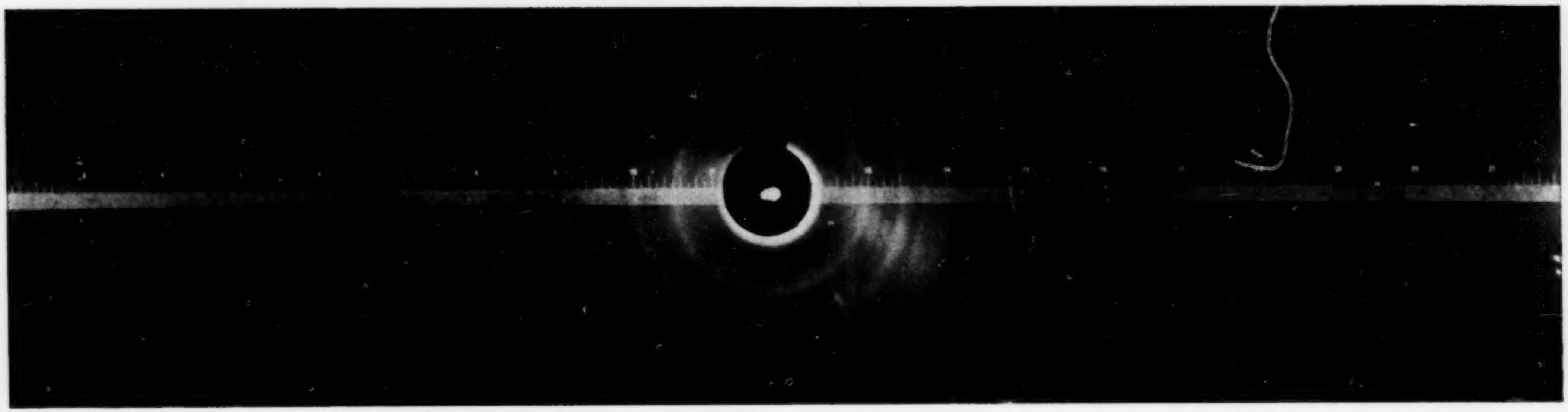

Fig. 3. Diagramme de diffraction aux rayons X du précipité *β* séché.

	Eau de constitution + quinoléine	MoO_3	SiO_2
Complexe α	23.70	73.39	2.90
Complexe β	23.79	73.55	2.65

ce qui correspond bien, dans les deux cas, à la formule globale:

$SiO_2.12\ MoO_3\ 4(C_9H_7N).\ 2\ H_2O$ - (Eau de constitution + quinoléine = 23.60%
(MoO$_3$ = 73.70%
(SiO$_2$ = 2.56%

$$\text{avec, comme facteur analytique: } \frac{\text{Précipité}}{\text{Si}} = 83.39$$

Etude aux rayons X

Les diagrammes Debye - Scherrer (raie Cu K α) font apparaître, au contraire, une différence de structure nette entre les deux types de précipités, comme le montrent les Figs. 2 et 3; il s'agit donc bien de deux formes isomères.

Propriétés analytiques des précipités

En raison de sa facilité de filtration, c'est la forme obtenue à partir du complexe β qui est la plus intéressante du point de vue analytique. Comme, d'autre part, c'est celle qu'on rencontre le plus fréquemment, c'est à elle seule que nous avons, par la suite, limité notre étude.

Mis à part le facteur analytique et la facilité de filtration, les propriétés importantes à connaître pour un dosage gravimétrique sont:

— la solubilité du précipité dans son milieu de formation et dans le liquide de lavage
— les conditions de séchage ou de calcination
— la reprise d'humidité.

Solubilité

Comme nous le verrons par la suite, le milieu de précipitation est un milieu chlorhydrique normal, comportant un excès de molybdate et un excès de quinoléine. La courbe 1 de la Fig. 4 se rapporte à la solubilité du précipité dans HCl normal, mesurée suivant le mode opératoire de l'annexe II. La présence de molybdate jusqu'à une concentration de 1% ne modifie pas sensiblement cette courbe. Par contre, l'addition de quinoléine entraîne une baisse rapide de la solubilité à froid, et même à chaud (courbes 2, 3, 4 - Fig. 4).

La solubilité du précipité dans l'eau est notable (courbe 1 — Fig. 5). Mais une faible concentration en quinoléine suffit à la rendre négligeable (courbes

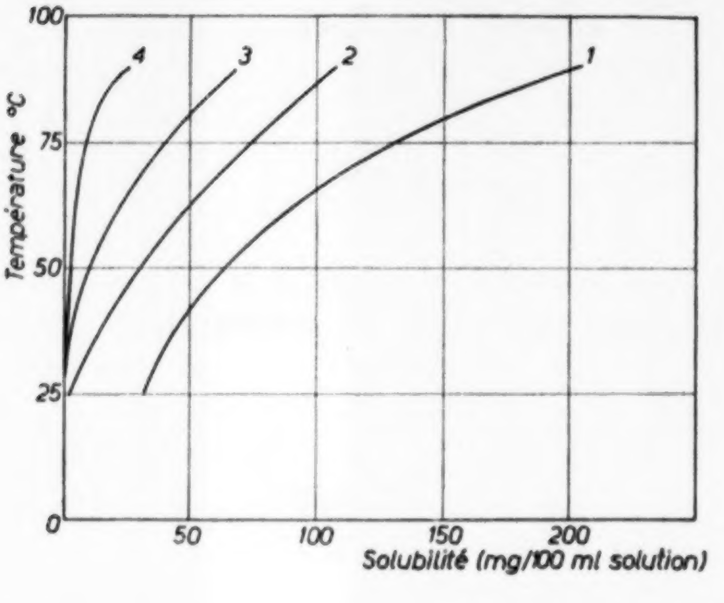

Fig. 4. Solubilité du précipité β dans HCl normal additionné de quinoléine, en fonction de la température.

Courbe 1. Concentration en quinoléine: 0.00%
Courbe 2. ,, ,, ,, : 0.05%
Courbe 3. ,, ,, ,, : 0.10%
Courbe 4. ,, ,, ,, : 0.20%

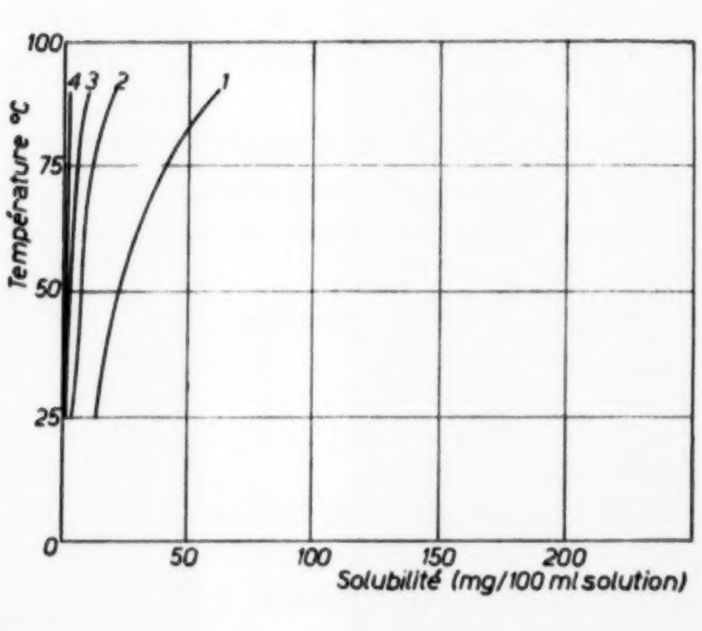

Fig. 5. Solubilité du précipité β dans l'eau additionnée de quinoléine en fonction de la température.

Courbe 1. Concentration en quinoléine: 0.00%
Courbe 2. ,, ,, ,, : 0.05%
Courbe 3. ,, ,, ,, : 0.10%
Courbe 4. ,, ,, ,, : 0.20%

2, 3, 4 — Fig. 5). Le lavage peut donc être effectué sans danger avec une solution de quinoléine à 0.05%. Il n'y a pas de surcharge occasionnée par la présence de quinoléine dans l'eau de lavage, car ce produit s'élimine complètement par évaporation au séchage.

Séchage

La courbe d'analyse thermogravimétrique de la figure 1 montre un palier entre 110 et 250°, correspondant au produit sec. Mais cette courbe a été enregistrée pour une vitesse de chauffage de 150°/heure. Pour une vitesse plus faible, la palier est atteint à une température beaucoup plus basse (60° pour 15°/heure). Le séchage est donc possible à toutes températures au-dessous de 250°. Nous avons déterminé le temps nécessaire à trois températures différentes, en pesant le précipité toutes les demi-heures. Les résultats de ces essais sont reportés sur la Fig. 6. La solution pratique est un séchage de une heure à 150°.

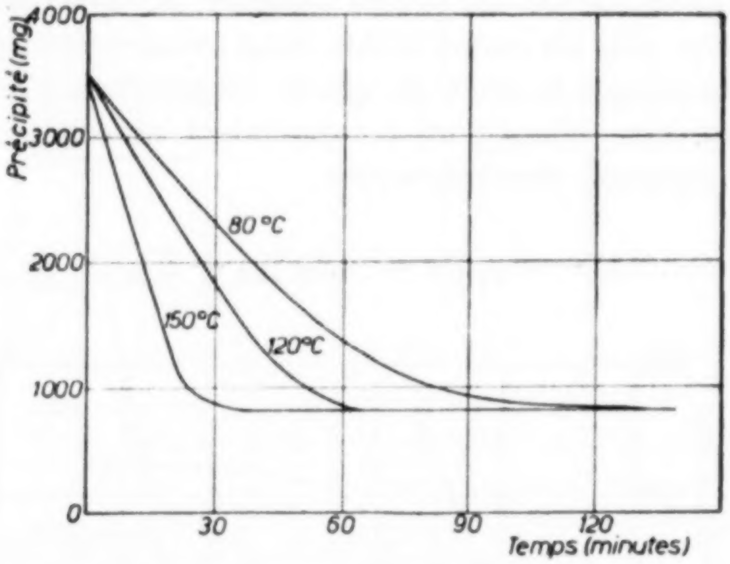

Fig. 6. Séchage du précipité à diverses températures.
Variation de poids du précipité en fonction du temps pour trois températures différentes.
Le précipité est introduit dans l'étuve amenée préalablement à la température voulue et celle-ci est maintenue constante pendant tout l'essai.

Reprise d'humidité

Le précipité ne reprend pas d'humidité au cours du refroidissement après séchage. On obtient les mêmes résultats en le refroidissant à l'air libre ou dans un dessicateur en présence de P_2O_5. Après refroidissement complet, le poids du précipité augmente lentement, mais la reprise d'humidité ne dépasse pas 0.5% au bout d'une heure; elle reste donc relativement faible.

Etude de la réaction de précipitation

Bien entendu, on ne peut précipiter la totalité du silicium présent en solution que si la réaction de formation du complexe silicomolybdique est elle-même complète, ce qui suppose réalisées un certain nombre de conditions que nous avons rappelées dans la première partie:

— concentration en Si inférieure à 100 mg au litre
— pH voisin de 1.0
— excès de molybdate

A priori, on peut supposer que les facteurs de précipitation sont:

— la concentration en molybdate, qui peut intervenir par son excès
— l'acidification après développement, nécessaire pour éviter la précipitation du molybdate en excès
— la concentration en quinoléine.

Pour étudier l'influence de ces divers facteurs, au lieu d'utiliser une liqueur synthétique de silice, plus ou moins stable, nous avons préféré partir de solutions provenant de l'attaque par la soude de quatre échantillons d'aluminium à teneur connue en silicium. Ces échantillons comprenaient un échantillon d'aluminium raffiné E_0 et 3 aluminium électrolytiques:

$$E_5 \text{ (Si} = 1.0\%) — E_{12} \text{ (Si} = 2.60\%) — E_{11} \text{ (Si} = 4.0\%).$$

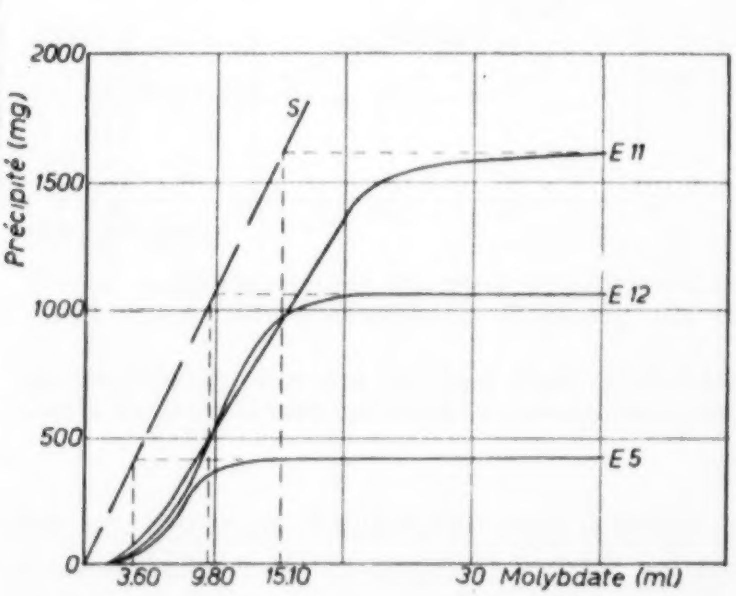

Fig. 7. Influence de la concentration en molybdate sur la précipitation du complexe β dans le cas de 3 échantillons à teneur variable en silicium.
En abscisse, sont indiquées les quantités stoechiométriques correspondant à la formation du complexe dans chacun des trois cas envisagés.

Echantillon E_5 (Si = 1.0%) → 3.60 ml de solution à 10%
E_{12} (Si = 2.6%) → 9.80 ,, ,, ,, ,, 10%
E_{11} (Si = 4.0%) → 15.10 ,, ,, ,, ,, 10%

La droite S est la droite stoechiométrique.

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Influence de la concentration en molybdate (mode opératoire: voir annexe IIIa)

La Fig. 7 montre que, pour obtenir la précipitation totale, il est nécessaire d'ajouter un excès de molybdate d'environ 15 ml de solution à 10 % pour 600 ml de solution, soit une concentration de 0.25 %. Cet excès correspond exactement à l'excès nécessaire pour obtenir le développement total du complexe. Il ne joue donc aucun rôle dans la précipitation elle-même; nous avons vu qu'il n'a également aucune action sur la solubilité du précipité.

Influence de l'acidification après développement (mode opératoire: voir annexe IIIb)

Nous avons dit qu'elle était nécessaire pour éviter la précipitation du molybdate en excès. On constate sur la Fig. 8 que la quantité minimum d'acide à ajouter est directement proportionnelle à l'excès de molybdate (4 ml d'acide chlorhydrique concentré par gramme de molybdate en excès).

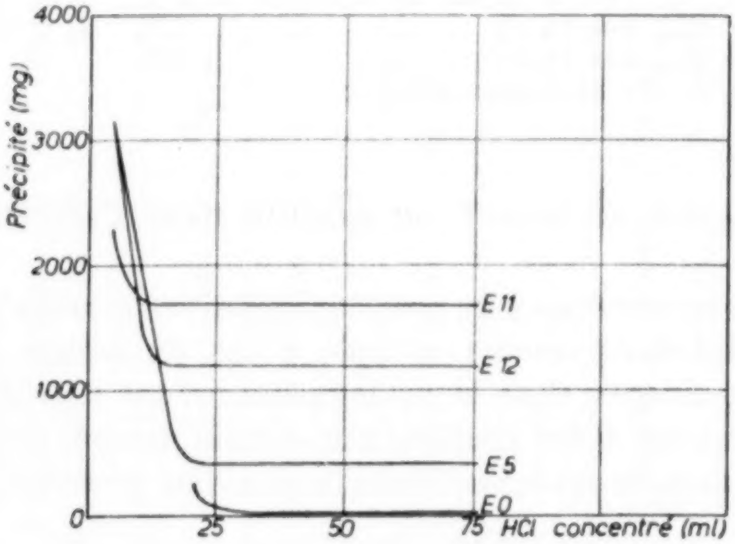

Fig. 8. Influence de la quantité d'acide sur la précipitation du complexe β, dans le cas de 4 échantillons à teneur variable en silicium.
E_0: aluminium raffiné, E_5, E_{12}, E_{11} = les mêmes que dans le cas de la Fig. 7.

Influence de la concentration en quinoléine (mode opératoire: voir annexe IIIc)

Là encore, la précipitation totale n'est obtenue qu'après addition d'un excès de 15 ml de quinoléine à 2 % pour 600 ml de solution, soit une concentration de 0.05 % (voir Fig. 9), c'est à dire, précisément la concentration nécessaire pour insolubiliser le précipité dans son milieu de formation.

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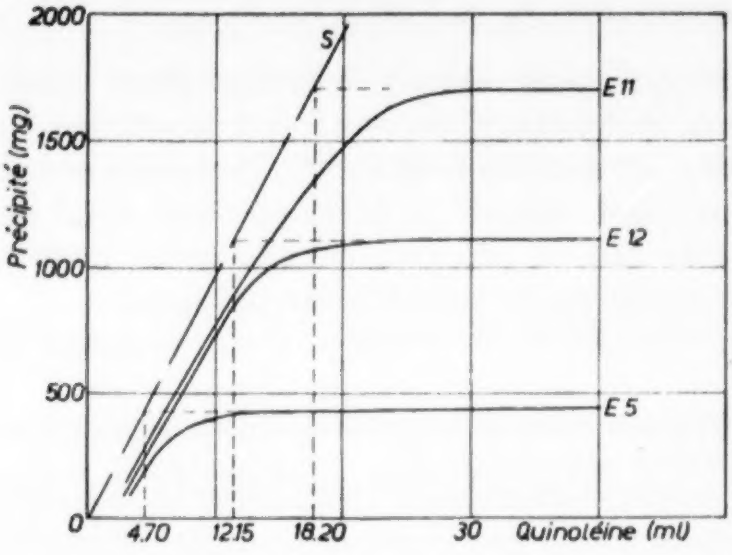

Fig. 9. Influence de la concentration en quinoléine sur la précipitation du complexe β dans le cas de 3 échantillons à teneur variable en silicium. (Mêmes échantillons que dans le cas de la Fig. 7.)

En abscisse, sont indiquées les quantités stoechiométriques correspondant à la précipitation du complexe dans chacun des 3 cas envisagés:

Échantillons E_5 → 4.70 ml de solution à 2%
E_{12} → 12.15 ,, ,, ,, ,, 2%
E_{11} → 18.20 ,, ,, ,, ,, 2%

La droite S est la droite stoechiométrique.

APPLICATION AU DOSAGE DU SILICIUM DANS L'ALUMINIUM

L'application de ces résultats à un problème défini ne présente aucune difficulté. Nous citerons simplement comme exemple le cas du dosage du silicium dans l'aluminium et ses alliages, dont le mode opératoire est reproduit dans l'annexe IV. Ce mode opératoire a été appliqué à un certain nombre d'échantillons d'aluminium — pour chacun de ces échantillons, nous avons procédé à la détermination de l'erreur moyenne $m = \sqrt{\frac{\Sigma e^2}{n - 1}}$ (n = nombre d'analyses — Σe^2 = somme des carrés des écarts par rapport à la moyenne).

Les valeurs de m obtenues sont groupées dans le tableau suivant:

Il est à noter que les écarts observés ne sont sans doute pas attribuables entièrement au mode opératoire, mais qu'ils peuvent en grande partie être dûs au manque d'homogénéité des échantillons. Ainsi, l'échantillon E_{15}, titrant 1.69% de silicium, présente une dispersion presque double de celle de l'échantillon E_{12} à 2.60%, alors que le contraire eût été logique si l'erreur provenait de la méthode de dosage. Le phénomène s'accentue, du reste, au stade des alliages (alpax ou hypersiliciés)

	$0.00 < Si < 0.25\%$ Prise d'essai: 5.000 mg Essai à blanc: 11 mg			$0.00 < Si < 2.50\%$ Prise d'essai: 1.000 mg Essai à blanc: 4 mg				$0.00 < Si < 25\%$ Prise d'essai: 100 mg Essai à blanc: 4 mg	
	E_0	E_{16}	E_{10}	E_{13}	E_{14}	E_{15}	E_{12}	E_{17}	E_{18}
Poids moyen de précipité P mg	28.7	286.9	792.5	239.5	352.6	1.413	2.177	1.064	1.782
m_P	3.1	1.7	2.5	3.1	2.9	11.2	6.5	9.9	67.8
Titre moyen T %	0.004	0.066	0.187	0.282	0.418	1.689	2.605	12.712	21.321
m_T	0.0007	0.0004	0.0006	0.0037	0.0034	0.0126	0.0077	0.118	0.81
$dT_{\max}$ 2 m_T	0.0015	0.0010	0.0010	0.0075	0.0070	0.0250	0.0150	0.235	1.62

pour lesquels l'homogénéité est encore plus difficile à réaliser. Dans ce cas, il y aurait certainement intérêt à augmenter la prise d'essai, quitte à n'effectuer la précipitation que sur une partie aliquote.

CONCLUSIONS

La précipitation du complexe silicomolybdique par la quinoléine permet, sans précautions spéciales, le dosage du silicium avec une précision de ± 0.1 mg. Cette méthode est entièrement comparable à la méthode colorimétrique, car elle est applicable aux mêmes domaines de concentration (0 à 100 mg de silicium par litre). Les deux méthodes se complètent avantageusement, car si la méthode gravimétrique est indispensable à l'étalonnage de la colorimétrie, elle ne peut par contre s'appliquer à des échantillons de trop faible importance. En outre, la précipitation conviendra particulièrement aux dosages isolés, alors que l'on aura recours plus volontiers à la colorimétrie pour les analyses en série.

Nous avons appliqué les deux méthodes avec succès, non seulement à l'aluminium, mais également aux matières premières nécessaires à son élaboration, en particulier aux produits fluorés. Il suffit, dans ce cas, de complexer le fluor par une quantité suffisante d'acide borique.

REMERCIEMENTS

Les auteurs tiennent à remercier particulièrement M. LOUDE, du Laboratoire d'UGINE, qui a bien voulu se charger des examens aux rayons X; MM. DU BELLAY ET TCHENG-KIEN du C. R. LYON, qui ont effectué les essais thermogravimétriques; et la Direction Générale de la S.E.C.E.M.A.E.U., qui a bien voulu autoriser la publication du présent mémoire.

ANNEXES

Annexe I

Développement et précipitation du complexe α

Ajouter 50 ml de paramolybdate d'ammonium à 10% dans 400 ml d'une solution contenant environ 20 mg de silicium et amenée à pH 3.50. Laisser le complexe α se développer 10 minutes, puis acidifier avec 50 ml HCl concentré, et précipiter en ajoutant 50 ml de solution chlorhydrique de quinoléine à 2% *.

Développement et précipitation du complexe β

Le mode opératoire est analogue au précédent, sauf que la solution de silice est acidifiée à pH 1.0 au lieu de pH 3.5.

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* Préparée par dissolution de 20 ml de quinoléine pure dans 50 ml HCl 1:2 et dilution à 1 litre avec de l'eau.

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Annexe II

Mesure de la solubilité du précipité dans une solution quelconque

Mettre en suspension 500 mg de précipité sec dans 100 ml de la solution considérée — Chauffer à 90° — Refroidir à la température voulue et l'y maintenir pendant quatre heures — Filtrer — Laver avec une solution de quinoléine à 0.05% *. Sécher une heure à 150° et peser.

Annexe III

Etude de l'influence de la concentration en molybdate

Attaquer 5.0 g d'échantillon par 50 ml de soude 10 *N*, en opérant dans un récipient en nickel. L'attaque terminée, reprendre par 134 ml d'acide chlorhydrique 10 *N*, et diluer à 2000 ml. Effectuer des prélèvements de 200 ml, que l'on dilue à 500 ml avec de l'acide chlorhydrique 0.14 *N*. Ajouter des quantités variables de solution de molybdate à 10%. Après 10 minutes de développement à froid, acidifier avec 50 ml d'acide chlorhydrique concentré, et précipiter par 50 ml de quinoléine à 2%. Filtrer — Laver avec la solution de quinoléine à 0.05% — Sécher une heure à 150° et peser.

Etude de l'influence de l'acidité après développement

Le mode opératoire est analogue à celui de l'annexe IIIa. Mais la variable est, cette fois, la quantité d'acide chlorhydrique concentré. Les quantités de molybdate et de quinoléine sont fixées à 50 ml.

Etude de l'influence de la concentration en quinoléine

Le mode opératoire est analogue à celui de l'annexe IIIa mais la variable est, cette fois, la concentration en quinoléine. Les quantités de molybdate et d'acide chlorhydrique concentré sont fixées à 50 ml.

Annexe IV

Dosage du silicium dans l'aluminium et les alliages d'aluminium

Prise d'essai : P mg (voir tableau)

Attaquer la prise d'essai dans un creuset ou une capsule en nickel, par A ml de soude 10 *N* — Terminer l'attaque sur plaque chauffante douce — Diluer à 100 ml environ et amener à l'ébullition** — Reprendre dans une fiole jaugée de 500 ml contenant B ml HCl 10 *N* — Diluer à environ 250 ml et chauffer en agitant jusqu'à dissolution complète, en se maintenant toujours au-dessous de l'ébullition — Refroidir et ajuster au trait — Transvaser dans un bécher de 800 ml — Ajouter 50 ml d'une solution à 10% de paramolybdate d'ammonium — Agiter et laisser la coloration se développer 10 minutes — Ajouter 50 ml HCl concentré et agiter — Si la solution est légèrement verte (réduction partielle du complexe jaune) réoxyder avec quelques gouttes de permanganate $N/10$ — Ajouter 50 ml de solution de quinoléine à 2% — Agiter, porter et maintenir quelques minutes à 80° — Refroidir complètement et filtrer sur creuset filtrant No. 4 — Laver six fois sur filtre avec une solution de quinoléine à 0.05% — Sécher une heure à 150° et peser après refroidissement à l'air libre.

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* Préparée par dilution de la solution à 2%.

** Dans le cas d'un alliage à haute teneur en silicium, ou contenant Cu ou Mg, ajouter 10 ml H_2O_2 10 volumes, en même temps que la soude, et prolonger l'ébullition jusqu'à élimination de l'eau oxygénée.

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Soit: T_1 = tare du creuset vide.
T_2 = tare du creuset + précipité après séchage.

$$\text{On a: Si \%} = \frac{T_1 - T_2}{83.39} \quad \frac{100}{P}$$

Teneur en silicium	P mg	NaOH 10 N A	HCl 10 N B
$2.50 < \text{Si} < 25\ \%$	100	12	20
$0.50 < \text{Si} < 2.50\ \%$	1.000	12	30
$0.00 < \text{Si} < 0.50\ \%$	5.000	35	100

RÉSUMÉ

Dans le présent travail, les auteurs ont étudié les conditions de précipitation du complexe silicomolybdique jaune par la quinoléine en vue du dosage du silicium.

Dans les conditions où le développement du complexe est total, la précipitation est elle-même quantitative en présence d'un excès de quinoléine, dont le rôle est d'insolubiliser le précipité dans son milieu de formation. On évite la précipitation du molybdate libre en ajoutant la quantité d'acide nécessaire à le complexer.

Le précipité ainsi obtenu filtre sans difficultés, et ne demande qu'un séchage de une heure à 150° pour atteindre un poids constant. Il correspond alors exactement à la formule: $SiO_2.12MoO_3.4(C_9H_7N).2H_2O$.

SUMMARY

The authors have studied the conditions of precipitation of complex silicomolybdic yellow by quinoline from the point of view of the determination of silicon.

Under the conditions that produce complete development of the complex, the precipitation is itself quantitative in the presence of an excess of quinoline, the role of which is to make the precipitate insoluble in its formation surroundings. The precipitation of free molybdate is prevented by adding the quantity of acid necessary for complexing it.

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The precipitate thus obtained filters without difficulty, and only needs to be dried for 1 hour at 150° in order to attain constant weight. It corresponds then exactly to the formula: $SiO_2.12MoO_3.4(C_9H_7N).2H_2O$.

ZUSAMMENFASSUNG

In der vorliegenden Arbeit untersuchten die Autoren im Hinblick auf die Bestimmung des Siliziums die Bedingungen der Ausfällung des gelben Siliziummolybdänkomplexes mit Quinolin. Unter den Bedingungen, bei denen die Bildung des Komplexes vollständig ist, ist in Gegenwart eines Überschusses von Chinolin die Ausfällung selbst quantitativ. Das Chinolin ist nötig um den Niederschlag im Bildungsmilieu unlöslich zu machen. Man vermeidet die Ausfällung von freiem Molybdat durch Zugabe der nötigen Menge Säure um es komplex zu binden.

Der so erhaltene Niederschlag wird ohne Schwierigkeiten filtriert und braucht nur eine Stunde bei 150° getrocknet zu werden um Gewichtskonstanz zu erreichen. Er entspricht dann genau der Formel: $SiO_2.12MoO_3.4(C_9H_7N).2H_2O$.

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EXTRACTION OF CATIONS AS SALTS OF FATTY ACIDS:

I. BERYLLIUM AS BUTYRATE

by

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INTRODUCTION

Liquid-liquid extraction of inorganic cations as an analytical tool is becoming increasingly popular especially when selectivity could be achieved by adjusting pH and other experimental conditions. In the course of a systematic investigation on the possibilities of extraction of metallic ions by organic solvents now in progress in these laboratories it is found that many of the cations are extracted by organic solvents in the presence of higher fatty acids like butyric acid and capric acid. WEST *et al.*[1] report the complete extraction of copper with benzene-butyric acid and ethyl acetate-capric acid in one extraction with only very few interferences. Beryllium has been extracted as basic acetate[2, 3, 4] and acetyl acetonate[5, 6] and the possibilities of these as analytical methods have been studied. This paper deals with the extraction of beryllium by organic solvents in the presence of butyric acid.

REAGENTS

Beryllium sulphate — B. D. H. AnalaR
Benzene
Carbon tetrachloride — B. D. H. L. R.
Amyl acetate
Chloroform
Ethyl Acetate — E. Merck
Butyric acid 80%
Ether — Alembic B. P.

EXPERIMENTAL

Beryllium sulphate is converted into chloride by double precipitation as hydroxide and dissolving in AnalaR hydrochloric acid. The strength of the stock solution, determined gravimetrically, is 3.07 mg as BeO/ml. A few experiments

References p. 529.

have also been carried out with a stock solution containing 2.60 mg of BeO/ml. 10 ml of the stock solution is mixed with an equal quantity of water and raised to the required pH. Ammonia is chosen for pH adjustments as better control is obtained at higher values, pH being measured with a Cambridge pH-meter. A known volume of butyric acid is added to this solution and is shaken well. 50 ml of the solvent is then added and the mixture shaken in a separating funnel for about 3-5 minutes. The aqueous layer is estimated for beryllium gravimetrically. The results are represented in Tables I to IV. Duplicate experiments carried out are reproducible to within 2% and the average values are reported.

DISCUSSION

Effect of pH

It is necessary to study the optimum conditions of pH at which the beryllium solution should be kept before the addition of butyric acid, at which maximum extraction can be effected. From a qualitative study it is observed that ethyl acetate and chloroform are the two best solvents among those tried and hence the effect of pH has been studied using chloroform as the solvent. It can be seen from Table I that below a pH of 7 the extraction is low and that between pH 9.3-9.5 there is maximum extraction corresponding to 90-94%. Hence this pH of 9.3-9.5 has been maintained in further studies.

TABLE I

Amount of Be for extraction = 30.7 mg as BeO
Solvent: Chloroform
Volume of solvent: 50 ml

Volume of Butyric acid in ml	% Extraction			
	pH 6.1	9.0	9.3	9.5
5	..	81	91	..
10	28	84	94	..
15	..	80	94	91
20	..	78	90	..
40	..	..	82	..

Solvents

The solvents tried are ethyl acetate, chloroform, benzene, carbon tetrachloride, ether and amyl acetate. The results are represented in Table II. It can be seen from the table that the solvents can be arranged in the order of their efficiency as: chloroform, ethyl acetate, ether, benzene, amyl acetate, carbon tetrachloride. The effect has also been studied at different concentrations of butyric acid.

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TABLE II

Volume of solvent: 50 ml
*Amount of Be for extraction = 26.0 mg

Vol. of Butyric acid in ml	% Extraction				
	Ethyl acetate	Ether*	Benzene	Amyl acetate	*Carbon tetra chloride
5	73+	80	59	51	14
10	75+	..	75	57	19
15	82	69	68	65	26
20	83	77	68	63	29

+pH = 9.0

TABLE III

No. of extractions	% Extraction
1	94
2	97
3	98
4	99

With chloroform the extraction is maximum (94%) with 10-15 ml of butyric acid. When the amount of fatty acid is increased, the amount of extraction decreases; as for example with 40 ml of acid the extraction decreases to 82%. With chloroform, a similar behaviour is observed at pH 9.0 (*vide* Table I). Amyl acetate and benzene behave similarly. With carbon tetrachloride and ether a different behaviour is observed. The extraction steadily increases with increase of butyric acid.

Chloroform being found to be the best solvent amongst those tried, attempts are made to extract beryllium completely by successive extractions and the results are tabulated in Table III. Identical conditions regarding pH, butyric acid concentration and volume of solvent are maintained for successive extractions. Maximum extraction achieved is 99%, with four extractions.

Effect of salts

TABLE IV

3 g of salt in the mixture	% increase in extraction
KCl	78
KNO_3	74
NH_4NO_3	30

References p. 529.

The effect of the presence of potassium chloride, potassium nitrate and ammonium nitrate on extraction has been studied. 10 ml of beryllium stock solution is mixed with 10 ml of 30% salt solution, pH raised to the desired value and extracted with chloroform and the aqueous layer is analysed for beryllium. It can be seen from Table IV that salts increase the efficiency of extraction possibly because of the salting-out effect.

Work is in progress with other fatty acids for the extraction of beryllium and also other metallic ions. This will be reported in a subsequent paper.

Thanks are due to Dr. J. SHANKAR and Dr. V. T. ATHAVALE, of Chemical Division, Atomic Energy Commission for their kind interest.

SUMMARY

The extraction of beryllium has been carried out in the presence of butyric acid. Of the solvents tried, *viz.*, ether, benzene, chloroform, amyl acetate, ethyl acetate and carbon tetrachloride, chloroform is found to be the best, ethyl acetate being the next. 30.7 mg of BeO in solution as chloride is raised to a pH of 9.3 to 9.5 to which 10-15 ml of butyric acid is added. Four extractions with chloroform extract 99% of beryllium.

RÉSUMÉ

L'extraction du béryllium a été effectuée en présence d'acide butyrique. Des solvants essayés: éther, benzène, chloroforme, acétate d'amyle, acétate d'éthyle et tétrachlorure de carbone, celui qui convient le mieux est le chloroforme, puis l'acétate d'éthyle. On porte au pH 9.3-9.5, 30.7 mg de BeO en solution chlorhydrique et on ajoute 10 à 15 ml d'acide butyrique. Quatre extractions au chloroforme permettent d'extraire 99% de béryllium.

ZUSAMMENFASSUNG

Die Extraktion von Beryllium wurde in Gegenwart von Buttersäure ausgeführt. Von den versuchten Lösungsmitteln, nämlich Äther, Benzol, Chloroform, Amylacetat, Ethylacetat und Tetrachlorkohlenstoff, wurde Chloroform als das beste und Äthylacetat als das nächst beste Lösungsmittel befunden. 30.7 mg BeO, das in der Lösung als Chlorid vorliegt, wurde auf ein pH von 9.3-9.5 gebraucht und mit 10-15 ml Buttersäure versetzt. Vier Extraktionen mit Chloroform extrahieren 99% des Berylliums.

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THE CHROMATOGRAPHIC EXAMINATION OF PERMISSIBLE FOOD DYES

by

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INTRODUCTION

The chromatography of wool dyes was carried out by ZAHN[1]; of acid, basic and neutral dyes by RAO, SHAH AND VENKATARAMAN[2]; of fluorescein and halogenated fluoresceins by GRAICHEN[3]; and of dyestuffs added to edible fats by THALER AND SCHELLER[4]; while the chromatographic examination of dyes used in U.S.A. for foods, drugs and cosmetics has recently been reviewed by TILDEN[5]. In this paper the authors describe the determination of the R_F values of the 36 food dyes permitted in the State of New South Wales, Australia, and the detection of these dyes in jelly crystals by partition chromatography on filter paper by the ascending technique.

EXPERIMENTAL

Drops measuring 0.01 ml approx. of 0.01 M aqueous solutions of the dyestuffs were placed by means of a platinum loop at distances of 2.5 cm apart along a pencilled line 3 cm from the bottom of a strip of filter paper (Munktell's 20/150) measuring 22 cm by 30 cm. The paper was formed into a cylinder and placed in a sealed jar containing the developing reagent and left in position for from 1 to 4 hours depending on the nature of the reagent used, the ascending technique of WILLIAMS AND KIRBY[6] being employed. Several developing reagents were tried and those found most satisfactory are listed in Table I.

TABLE I

DEVELOPING REAGENTS USED IN EXPERIMENTAL WORK WITH PAPER PARTITION CHROMATOGRAPHY OF PERMISSIBLE FOOD DYES

1. Ethanol (95%), 250 ml; pyridine, 25 ml; 10 N HCl, 32 ml.
2. Ethylenediamine, 10 ml; water, 5 ml; butanol, 85 ml.
3. Phenol, 66 g; water, 32 ml; formic acid, 2 ml.
4. Phenol, 150 g; water, 48 g; glacial acetic acid, 2 g. (TILDEN[5]).

The R_F values obtained from aqueous dye solutions with various developing reagents are shown in Table II. In calculating these values, the distance travelled by the spot was measured from the base line to the point of maximum color intensity of the spot. The numbers assigned to the dyestuffs examined are those given in Rowe's Colour Index[7].

TABLE II

R_F VALUES GIVEN WITH VARIOUS DEVELOPING REAGENTS ON AQUEOUS DYE SOLUTIONS

Color of dye	Color Index No.	R_F values in developing reagent No.			
		1≠	2	3	4
Red	31	D	Nil	0.54	0.38
,,	57	D (0.30)	,,	0.63	0.42
,,	79	C	0.92	0.54	0.34
,,	80	C	Nil	0.52	0.34
,,	Ponceau S X	C	,,	0.55	0.43
,,	85	C	,,	0.50	0.42
,,	179	C	,,	0.47	0.46
,,	184	D	Nil (dec.)	0.18	0.07
,,	185	D	Nil	0.40	0.09
,,	225	D	,,	0.55	0.45
,,	677	B	0.93+	0.98+	0.98+
,,	749	A	0.97+	0.98+	0.98+
,,	771	B	0.75	0.92+	0.95+
,,	773	B	0.80	0.94+	0.98+
,,	777	B	0.83	0.93+	0.96+
Orange	150	C	0.93	0.74	0.78
,,	151	C	0.88	0.82	0.78
Yellow	10	C	Nil	0.60	0.28
,,	22×	A	1.0	1.0	0.96+
,,	61×	A	1.0	1.0	0.98+
,,	Sunset yellow FCF	C	dec.	0.54	0.31
,,	640	C	,,	0.16	0.05
,,	655	B	0.98+	0.98+	0.97+
Green	662	B	0.96+	0.98+	0.95+
,,	666	B	0.67	1.0	0.94+
,,	670	C	dec.	0.71	0.60
Blue	289	D	0.81	0.93+	0.80
,,	518	Nil	Nil	0.09	0.02
,,	661	B	0.67 dec.	1.0	0.95+
,,	Brilliant blue FCF	B	Trails to 0.7	0.82+	0.72
,,	707	O	dec.	0.92+	× ×
,,	861×	A	1.0	0.98+	0.99+
,,	1180	D (dec.)	dec.	0.42	0.12
Brown	331	D	0.98+	1.0	0.95+
Violet	680	B	0.97+	0.98+	0.99+
Black	865	Nil	Nil	× ×	× ×

Footnote to Table II

× : Oil soluble dyes (dissolved in ethyl acetate).
+ : Travels to liquid front.
× × : Trails to liquid front.
O : Tails from base line to liquid front.
Dec.: Decolorised.
≠ : This reagent gives three liquid fronts, *viz*:
A : The dye travels at the first liquid front
B : The dye travels between the first two liquid fronts (R_F values 0.8 to 1.0 approx.)
C : The dye travels at the second liquid front (R_F values 0.8 approx.)
D : The dye travels between the base line and the second liquid front (R_F values 0 to 0.8).
There is a third front at approximately R_F value 0.6.

The R_F values obtained on extracting aqueous solutions of the dyes with butanol saturated with 2 *N* HCl and developing with various reagents are shown in Table III. All the dyes examined were soluble in this mixture, excepting No. 865, which was only sparingly soluble.

TABLE III

R_F VALUES OF DYES EXTRACTED WITH BUTANOL SATURATED WITH 2 *N* HCl AND DEVELOPED WITH VARIOUS REAGENTS

Color of dye	Color Index No.	R_F values in developing reagent No.			
		1≠	2	3	4
Red	31	C	0.11	0.46	0.22
,,	57	D	0.04	0.57	0.21
,,	79	C	0.42	0.48	0.41
,,	80	C	0.38	0.48	0.41
,,	Ponceau S X	C	0.28	0.58	0.47
,,	85	C	0.06	0.56	0.37
,,	179	C	0.10	0.61	0.42
,,	184	C	0.05	0.24	0.11
,,	185	C	0.02	0.35	0.18
,,	225	C	0.06	0.60	0.37
,,	677	A	0.98+	0.98+	0.94+
,,	749	A	0.97+	0.98+	0.94+
,,	771	A	0.82	0.96+	0.92+
,,	773	B	0.80	0.96+	0.94+
,,	777	A	0.68	0.92+	0.93+
Orange	150	B	0.91	0.84	0.76
,,	151	B	0.88	0.84	0.84
Yellow	10	C	0.13	0.60	0.38
,,	22×	—	—	—	—
,,	61×	—	—	—	—
,,	Sunset yellow FCF	C	0.07	0.52	0.42
,,	640	C	Nil	0.28	0.19
,,	655	A	0.98+	0.98+	0.94+

References p. 537.

Color of dye	Color Index No.	R_F values in developing reagent No.			
		1≠	2	3	4
Green	662	A	0.99+	0.96+	0.96+
,,	666	A	0.75	0.96+	0.93+
,,	670	B	dec.	0.78	0.60
Blue	289	A	0.23	0.90+	0.80
,,	518	D (0.11)	0.05	0.05	0.03
,,	661	A	dec.	0.96+	0.93+
,,	Brilliant blue FCF	D (0.15)	dec.	0.88+	0.03
,,	707	B	0.78	0.94+	0.88+
,,	861×	A	0.97+	1.0	0.95+
,,	1180	D	dec.	0.36	0.28
Brown	331	A	0.98+	0.96+	0.98+
Violet	680	A	0.97+	1.0	0.97+
Black	865	A and C	Nil	0.32	0.32+

See footnote, Table II, p. 532.

A jelly crystal mixture was made by mixing 17 g gelatin, 91 g sucrose and 1 g citric acid. A few drops of aqueous 0.01 *M* solution of the individual dyes were added to 1 g samples of this mixture and extracted by warming with 5 ml butanol saturated with 2 *N* HCl. Drops of this extract were spotted on and developed with reagent No. 3 with results as shown in Table IV.

TABLE IV

R_F VALUES OBTAINED BY EXTRACTING COLORED JELLY CRYSTAL MIXTURES WITH BUTANOL SATURATED WITH 2 *N* HCl AND DEVELOPING WITH REAGENT No. 3 (Phenol-water-formic acid).

Color of dye	Color Index No.	R_F Value
Red	31	0.44
,,	57	0.46
,,	79	0.44
,,	80	0.36
,,	Ponceau S X	0.47
,,	85	0.29
,,	179	0.38
,,	184	0.32
,,	185	0.36
,,	225	0.51
,,	677	0.93+
,,	749	0.96+ (tails from 0.54)
,,	771	0.68+
,,	773	0.76+
,,	777	0.94+

Color of dye	Color Index No.	R_F Value
Orange	150	0.76
,,	151	0.72 (tails from 0.40)
Yellow	10	0.64
,,	Sunset yellow FCF	0.72
,,	640	0.37
,,	655	0.94+
Green	662	0.96+
,,	666	0.90+
,,	670	0.66
Blue	861	0.97+
,,	289	0.98+
,,	518	0.10
,,	661	0.98+
,,	Brilliant blue FCF	0.83
,,	707	0.84 (tails from 0.1 to liquid front)
,,	1180	0.39
Violet	680	0.98+
Brown	331	0.96+
Black	865	0.90+

+ Travels to liquid front.

The following color changes were noted on extraction with butanol saturated with 2 N HCl: —

Color of original dye	Color index No.	Color changed to
Red	677	Blue-red
,,	749	Pale red (fluorescent)
,,	771	Yellow
,,	773	Orange
,,	777	,,
Blue	1180	Slight blue-green
Black	865	Very little extracted

Nine samples of commercial jelly crystals were examined by extracting 1 g samples with 5 ml of warm butanol saturated with 2 N HCl and developing the extracts so formed with reagent No. 3. The results obtained, which were confirmed by the manufacturer, are shown in Table V.

References p. 537.

TABLE V

R_F VALUES OF DYESTUFFS IN COMMERCIAL JELLY CRYSTALS EXTRACTED WITH BUTANOL SATURATED WITH 2 N HCl AND DEVELOPED WITH REAGENT No. 3

Type of Jelly Crystal	Index Numbers of colors extracted
Cherry	179
Lime	640 and 670
Raspberry	179
Strawberry	179
Black Currant	184 and 1180
Red Currant	179
Pine	640
Lemon	640
Orange	151

Mixtures of 0.01 M aqueous solutions of the dyes were made and drops of the various blends separated by development as shown in Table VI.

TABLE VI

SEPARATION OF DYES FROM VARIOUS MIXTURES

Color Index numbers of dyes in mixture				Developing reagent No.
749	80	185		1
640	662	225		
771	10	57		
666	670	518		
771	150	331		
749	771	179		2
662	151	518		
655	773	771		
331	150	289		
680	771	865		
150	57	184		3
677	289	1180		
151	185	640	518	
749	79	184		
22	10	640		
655	10	184		

The two-dimensional separation of dyes was not seriously applied to this examination, but it is proposed to embody it in the separation of individual dyes from their respective color groups in a further investigation.

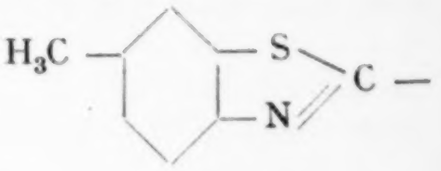
DISCUSSION

As a result of the work carried out the following general conclusions may be drawn: —

1. The phenol-water-acetic acid mixture (reagent No. 4) used by TILDEN[5] was found to be satisfactory, but better results were obtained with that used by the authors when formic acid was substituted for acetic acid (reagent No. 3), higher R_F values being given and the spots obtained less subject to "tailing".
2. The extraction of the dyestuffs contained in jelly crystals with warm butanol saturated with 2 *N* HCl is a satisfactory method for detecting the coloring matter present, provided that the concentrations of the components of the color mixtures are of a comparable order of magnitude. When the concentration of one dye greatly exceeds that of another in a mixture, their separation is difficult, particularly if they be of the same color, *e.g.* the separation of yellow dye No. 10 from dye No. 640, is only possible when their ratio is not greater than 1 to 10.
3. The R_F values obtained with various dyes vary with the method of extraction employed and the developing reagent used. Samples of unknown dye mixtures should, therefore, be compared with known mixtures of approximately the same dye concentration by the application of similar methods of extraction and development.
4. The structure of the monazo dyestuffs has an effect on the R_F values obtained, a decrease in the number of acid groups giving an increase in R_F value. Development of aqueous dye solutions with reagent No. 3 (phenol-water-formic acid) showed the following relationship: —

Number of sulphonic groups	R_F values	Color Index Nos. of dyes
3	0.2 to 0.4	185, 184
2	0.4 to 0.65	Sunset yellow FCF, 179, 31, 57, 79, 80, 85, Ponceau S X
1	0.6 to 0.85	150, 151, 225
Nil	0.85 to 1.0	22, 61

The substituent groups, CH_3 and $NH.COCH_3$, apparently have no effect on the R_F values obtained, nor does the position of the SO_2OH groups. The deviation of dye No. 225 from the general rule may be due to the group



which is attached to the benzene nucleus of this dye.

References p. 537.

5. The identification of some of the dyes, *viz.* Nos. 225, 707, 755, 749, 771, 773, 777 and Ponceau S X may be checked by the fact that their spots fluoresce under ultraviolet light. The fluorescence of Nos. 749, 771, 773 and 777 has the same color as that of the acid solution of the dye, while No. 707 gives a blue-green fluorescence. The others have approximately the same colors as their aqueous solutions.

SUMMARY

The R_F values of 36 permissible food dyes have been determined by partition chromatography on filter paper. The detection of these colors in jelly crystals has been investigated and a method for their extraction and development described. A relationship between dye structure and R_F value has been suggested.

RÉSUMÉ

Les valeurs de R_F de 36 colorants alimentaires ont été déterminées par chromatographie de partage sur papier filtre. La détection de ces colorants dans les gelées a été examinée et une méthode d'extraction est décrite. On peut admettre qu'il y a une relation entre la structure d'un colorant et sa valeur de R_F.

ZUSAMMENFASSUNG

Die R_F-Werte von 36 zulässigen Lebensmittelfarben wurden mit Hilfe der chromatographischen Trennung auf Filterpapier untersucht. Die Auffindung dieser Farben in Geleekristallen wurde untersucht und eine Methode zur Extraktion und Entwicklung beschrieben. Eine Beziehung zwischen der Farbstoffstruktur und dem R_F-Wert wurde vermutet.

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DOSAGE D'OXYDES DE TANTALE, NIOBIUM ET TITANE DANS LEURS MÉLANGES PAR RADIOACTIVITÉ

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Les méthodes habituelles de dosage des éléments tantale, niobium et titane dans leurs mélanges sont longues, délicates et peu précises. On utilise couramment leur précipitation par le tannin à des pH différents, suivie de la calcination des précipités et de la pesée des oxydes. Le titane se partage entre le précipité de tantale et celui de niobium; il est dosé colorimétriquement après mise en solution des oxydes. La séparation tantale-niobium obtenue ainsi est très mauvaise car le niobium est entraîné en partie sur le précipité de tantale et réciproquement. Pour y remédier on doit effectuer plusieurs précipitations successives du tantale en s'arrêtant lorsque le poids d'oxydes obtenu est constant, d'où de longues manipulations et des risques de pertes.

Nous avons cherché à doser ces éléments avec l'aide de traceurs radioactifs. Deux méthodes se sont révélées possibles:

— 1) le dosage par activation du mélange

— 2) la séparation au tannin après addition de niobium radioactif.

DOSAGE PAR ACTIVATION

Activités induites

Par irradiation aux neutrons thermiques d'un mélange Ta-Nb-Ti on obtient les isotopes radioactifs suivants:

Elément	Masse	Période	Section eff. (barns/atome)	Energie du rayonnement en MeV	
				béta	gamma
Nb	94	6.6 min	1.4	1.3 (0.1%)	0.045
Ta	182	16.4 min	0.034	0.2	0.18
	182	117 j.	21	0.5	1.2-0.2
Ti	51	6 min	0.007	1.6	—

Méthode

Le tantale peut être dosé après irradiation du mélange en mesurant la radioactivité induite parce qu'il donne seul un isotope radioactif de période longue et de grande section efficace. Le titane peut ensuite être dosé par colorimétrie. On obtient le niobium par différence.

Le mélange d'oxydes à analyser est irradié à la pile dans un tube en aluminium en même temps et dans les mêmes conditions qu'une quantité connue d'oxyde de tantale pur qui sert d'étalon. Le niobium et le titane absorbent suffisamment peu les neutrons pour que l'on puisse considérer que l'échantillon et l'étalon de tantale sont soumis au même flux.

Vingt quatre heures après l'irradiation les activités de l'échantillon et du témoin sont mesurées et comparées, ce qui indique la quantité de tantale présente dans le mélange à analyser. Pour cette mesure un certain nombre de précautions sont nécessaires.

Mesure des activités

Les deux poudres doivent être montées de façon identique pour pouvoir être comparées avec le minimum d'erreur. En particulier, elles doivent être d'épaisseur uniforme. On peut y parvenir en mettant les poudres en suspension dans l'alcool et en filtrant sur papier au moyen d'un entonnoir démontable[1]. Le dépôt obtenu est assez homogène. On peut ensuite monter le papier filtre sur un carton rigide.

Les mesures sont faites au compteur de Geiger du type „cloche" avec fenêtre mince à la partie inférieure. Le rayonnement β de ^{182}Ta étant peu énergique est en partie absorbé dans l'épaisseur de la source. Cette self-absorption introduit une erreur si toutes les sources n'ont pas la même épaisseur. Pour y remédier on mesure le rayonnement γ seul après absorption du rayonnement β à travers un écran de 500 mg/cm^2. Le résultat de la mesure est alors indépendant de la masse superficielle de la source comme nous l'avons vérifié entre 10 et 50 mg/cm^2.

Résultats

On peut par cette méthode doser de faibles quantités de tantale. En effet une irradiation de 275 heures au flux de $5 \cdot 10^9$ neutrons/cm^2/seconde conduit, dans nos conditions de mesure, à une activité de 1,000 coups/min par mg de Ta, ce qui est aisément mesurable.

Des essais ont été faits sur des mélanges connus. On a dosé 0.1 mg de tantale avec une précision de l'ordre de 10% dans des mélanges d'oxydes de tantale et de niobium à 1% et 5% de Ta_2O_5.

Les résultats obtenus par cette méthode dans le dosage d'un mélange provenant d'un minerai sont résumés plus loin.

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[1] P. SÜE, *Ann. chim. anal.*, 24 (1942) 204.

DOSAGE PAR ADDITION DE NIOBIUM RADIOACTIF

Cette méthode est un perfectionnement de la séparation par le tannin dont nous avons exposé plus haut les inconvénients.

Principe de la méthode

A la solution de Ta-Nb-Ti à doser on ajoute d'abord du niobium radioactif ^{95}Nb d'activité spécifique aussi élevée que possible. On précipite ensuite le tantale par le tannin à un pH où cette précipitation est complète, puis le niobium est précipité dans le filtrat à un pH plus élevé. Dans ces conditions une partie du niobium se retrouve dans le premier précipité, le reste dans le second. L'addition préalable de ^{95}Nb permet de mesurer comment ce partage s'est effectué et d'introduire une correction. Le titane est dosé après calcination sur les oxydes remis en solution.

Le niobium radioactif ^{95}Nb a une période de 35 jours. Il émet un rayonnement β de 0.146 MeV et un rayonnement γ de 0.758 MeV. On l'obtient à partir des produits de fission de l'uranium.

Nous avons étudié d'abord la précipitation du tantale seul, puis en présence de niobium et enfin en présence de niobium et de titane. Des dosages ont ensuite été faits sur des mélanges connus et inconnus.

Essais effectués

Précipitation du tantale seul

L'influence du pH sur la précipitation a été étudiée dans les conditions suivantes:

Pour 100 à 200 mg d'oxydes, on emploie un volume de 250 ml contenant 8 g d'oxalate d'ammonium et 10 g de chlorure d'ammonium. Le pH est ajusté à la valeur choisie par SO_4H_2 ou NH_4OH. La précipitation est faite à chaud par une solution aqueuse de tannin à 2% dont on utilise 30 ml pour 100 mg d'oxydes.

On est parti d'une solution obtenue par fusion, avec 15 fois son poids de bisulfate de potassium, de Ta_2O_5 irradié à la pile et contenant l'isotope actif ^{182}Ta. Cette solution est étalonnée en poids par précipitation au tannin à pH 6 et pesée de Ta_2O_5 après calcination. Elle est également étalonnée en activité soit à l'aide d'un compteur à immersion *, soit par mesure au compteur cloche de Ta_2O_5 obtenu lors du dosage.

On a effectué des précipitations à différents pH en mesurant à chaque fois la quantité de tantale restant dans le filtrat. Cette mesure était faite soit au compteur à immersion, soit en ajoutant à nouveau du tantale au filtrat et en le reprécipitant en milieu plus alcalin (pH 6).

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* On a vérifié que l'activité due au potassium radioactif naturel de SO_4HK était négligeable devant celle de ^{182}Ta.

On a tracé la courbe du % de tantale non précipité en fonction du pH. Elle montre qu'il faut se placer à pH 3.8 pour que le tantale précipite complètement à 1% près.

A pH 3.7, il reste 1.6% de tantale non précipité et à pH 4, 0.2%.

Précipitation du tantale en présence de niobium

Les essais précédents ont été répétés en présence de niobium non radioactif en ramenant toutes les quantités de réactifs à 100 mg d'oxydes totaux.

Le tantale a été précipité au pH choisi et le niobium restant a été précipité à pH 6. La mesure de la radioactivité a permis de connaître la quantité de tantale non précipitée, ou plus exactement précipitée avec le niobium. La pesée des deux précipités a permis d'évaluer quelle proportion du niobium passe dans le tantale. Les résultats sont portés sur le Tableau I.

Il est à remarquer qu'une faible erreur sur la détermination du pH suffit à expliquer la dispersion des résultats.

La conclusion de ces essais est que la précipitation du tantale ne paraît pas affectée par la présence du niobium et que d'autre part il vaut mieux effectuer la précipitation à pH 3.8 qu'à pH 4 pour diminuer l'entraînement du niobium.

Précipitations à pH 3.8			Précipitations à pH 4		
$\frac{Nb_2O_5}{Ta_2O_5}$	% Nb_2O_5 dans Ta_2O_5	% Ta_2O_5 dans Nb_2O_5	$\frac{Nb_2O_5}{Ta_2O_5}$	% Nb_2O_5 dans Ta_2O_5	% Ta_2O_5 dans Nb_2O_5
0	—	1.0	0	—	0.5
1	16.4	0.7	1	41.7	0.4
	11.1	1.2			
			2	44.5	0.15
2	18.4	0.7			
	11.3	1.7	3	39.1	0.25
	14.2	0.7			
	19.2	0.8	moyenne	42.0	0.25
3	25.4	1.0			
	12.3	1.6			
moyenne	16.0	1.1			

Précipitation de mélanges tantale, niobium, titane

Il a été effectué des essais de précipitation à pH 3.8 analogues aux précédents mais avec la présence supplémentaire de titane dans le mélange, toujours dans le but de vérifier si la précipitation du tantale est complète.

Pour un rapport $Nb_2O_5/Ta_2O_5 = 1.5$ et des quantités variables de titane, en a trouvé:

% de TiO_2	% Ta_2O_5 dans Nb_2O_5
6.4	0.6
12.1	0.6
17.0	1.4

La présence de titane dans les proportions étudiées ne modifie donc pas sensiblement la précipitation du tantale. Il faut cependant tenir compte de ce que la précipitation du titane consomme du tannin. Si celui-ci est ajouté en quantité insuffisante la précipitation du tantale est moins complète comme le montrent les résultats suivants:

Poids total d'oxydes (mg)	Ta_2O_5 (mg)	Nb_2O_5 (mg)	TiO_2 (mg)	Tannin à 2% (ml)	% de Ta non précipité
148.7	59.7	79.5	9.5	30	0.93
157.2	59.7	79.5	19.0	30	2.7
148.7	59.7	79.5	9.5	45	0.6
158.2	59.7	79.5	19.0	47	0.6
167.7	59.7	79.5	28.5	50	1.4

MODE OPÉRATOIRE

A partir des essais précédents, le mode opératoire suivant a été adopté:

Les oxydes à doser sont mis en solution par fusion dans un creuset de platine avec 10 à 15 fois leur poids de bisulfate de potassium. La masse fondue est reprise par une solution d'oxalate d'ammonium à 4% et on lui ajoute 1 ml de la solution de ^{95}Nb. Les solutions utilisées habituellement étaient des solutions oxaliques renfermant 0.5 mg de Nb_2O_5/ml avec une activité de 3.000 coups/min/ml mesuré à travers un écran de 500 mg/cm².

Pour 100 à 200 mg d'oxydes on amène à 250 ml de solution contenant 8 g d'oxalate d'ammonium et 10 g de chlorure d'ammonium. On porte à pH 3.8 par addition de SO_4H_2. On précipite à chaud en ajoutant 30 ml de solution aqueuse fraîchement préparée de tannin à 2% par 100 mg d'oxydes totaux. On fait bouillir 2 minutes et laisse reposer 1h30. On filtre et lave avec une solution chaude de NH_4Cl à 2% jusqu'à disparition des ions SO_4^{-2} dans le filtrat. Le précipité est calciné à 900° et pesé.

Le filtrat est concentré au volume initial et porté à pH 6. On lui ajoute 60 ml de solution de tannin pour précipiter le niobium. Le précipité est lavé, filtré, calciné et pesé comme précédemment.

Une partie de chaque précipité est pesée et remise en solution pour y doser le titane par colorimétrie (environ 95% du titane se retrouve dans Ta_2O_5).

Le reste du précipité est pesé et monté sur un porteur de source pour la mesure au compteur qui est effectuée à travers un écran de 500 mg/cm².

Calcul des résultats

Soient: x et y les poids réels de Ta_2O_5 et Nb_2O_5 dans le mélange

p et p' les poids trouvés pour les deux précipités après déduction de TiO_2 dosé par ailleurs.

n et n' les activités des deux précipités.

Le rapport $n/n+n'$ représente la fraction a du niobium qui a précipité avec le tantale. Si l'on admet que 1% du tantale précipite avec le niobium on peut écrire:

$$p = 0.99\ x + ay$$
$$p' = 0.01\ x + (1-a)\ y$$

D'où l'on tire

$$y = \frac{p' - 0.01\,(p + p')}{0.99 - a}$$

$$x = (p + p') - y$$

L'erreur sur y (poids de Nb_2O_5) est d'autant plus faible que a est plus faible, c'est-à-dire que l'entraînement de niobium avec le tantale est moins grand.

L'erreur sur x (poids de Ta_2O_5) est d'autant plus faible que le rapport Nb_2O_5/Ta_2O_5 est plus faible. Si ce rapport est grand on a intérêt à doser le tantale par activation. Sinon le dosage par addition de ^{95}Nb est plus précis.

RÉSULTATS

Dosage dans des mélanges connus

Les résultats obtenus sur des mélanges synthétiques sont résumés dans le Tableau II.

TABLEAU II

Rapport	TiO_2	Introduits (mg)			trouvés (mg)			a	Erreur % sur	
Nb_2O_5/Ta_2O_5	%	Ta_2O_5	Nb_2O_5	TiO_2	Ta_2O_5	Nb_2O_5	TiO_2		Ta	Nb
0.8	0	50.0	41.1	0	50.6	41.0	0	0.222	+1.2	—0.25
1.7	13	48.5	81.5	20	48.2	81.4	20	0.188	—0.6	—0.3
3.2	0	49.6	159.0	0	51.0	155.9	0	0.149	+2.8	—2.0
6.3	6.5	19.3	120.9	10	20.1	120.3	10	0.326	+4.0	—0.5

Dosage dans un minerai

3 portions de 500 mg de minerai ont été traitées pour en extraire le mélange des oxydes de Ta, Nb et Ti. Sur chacune des fractions d'oxydes les 3 éléments ont été dosés. Les résultats sont portés dans le Tableau III.

TABLEAU III

n° des fractions		1	2	3	4
Poids d'oxyde totaux (mg)		373	365	365	368.2
Dosage par addition de ^{95}Nb					
% Ta_2O_5		13.9	14.5	14.2	14.7
% Nb_2O_5		52.3	52.9	53.1	52.1
% TiO_2		7.0	5.5	5.7	6.6
Dosage par activation					
% Ta_2O_5	(a		13.3	15.9	14.7
	(b	13.0			14.6—13.7
	(c	16.7			14.8

a) Oxydes irradiés directement
b) Oxydes irradiés en solution
c) Oxydes irradiés après mise en solution et reprécipitation par le tannin.

Conclusions

Les résultats obtenus sur le minerai par addition de ^{95}Nb concordent bien dans l'ensemble. Les résultats obtenus par activation sont plus divergents. Ceci peut être dû à la présence d'éléments autres que Ta, Nb ou Ti dans les oxydes irradiés. En effet on trouve en général pour le tantale des résultats plus forts par cette dernière méthode ce qui peut s'expliquer par la présence d'une activité parasite.

Les auteurs remercient Monsieur J. Huré qui a suggéré l'emploi de ^{95}Nb et a été l'initiateur de cette étude.

RÉSUMÉ

Les oxydes de niobium, tantale et titane peuvent être dosés dans leur mélange au moyen des traceurs radioactifs. Deux méthodes ont été étudiées:

1ère méthode. Par irradiation du mélange aux neutrons lents et mesure de l'activité du ^{182}Ta formé, on peut doser le tantale à 10% près dans des mélanges pauvres en cet élément.

2ème méthode. C'est un perfectionnement du procédé classique de séparation de ces oxydes par le tannin. A la solution à doser on ajoute du niobium radioactif ^{95}Nb d'activité spécifique connue, puis le tantale est précipité par le tannin à pH

3.8 ainsi qu'une partie du niobium. Le niobium est ensuite précipité dans le filtrat à un pH plus élevé. La mesure de l'activité des deux fractions permet de connaître comment le partage s'est effectué et d'introduire la correction nécessaire. Le titane est dosé par colorimétrie après calcination sur les oxydes remis en solution.

SUMMARY

The oxides of niobium, tantalium and titanium can be determined in their mixtures by means of radioactive tracers. Two methods have been studied.

1st method. On irradiation of the mixture with slow neutrons and measuring the activity of the ^{182}Ta formed, tantalium can be determined within about 10% in mixtures poor in this element.

2nd method. It is an improvement of the classical method of separation of these oxides by tannin. ^{95}Nb of known specific activity is added to the solution to be determined, then tantalium, together with a part of the niobium, is precipitated by tannin at pH 3.8. Niobium is then precipitated in the filtrate at a higher pH. The activity measurement of the two fractions allows the determination of how the partition is effected and the introduction of the necessary correction. Titanium is determined by colorimetry after calcination of the redissolved oxides.

ZUSAMMENFASSUNG

Die Oxyde von Niob, Tantal und Titan können in ihren Mischungen mit Hilfe von radioaktiven Spuren bestimmt werden. Es wurden 2 Methoden untersucht:

1. Methode. Durch Bestrahlen der Mischung mit langsamen Neutronen und Messung der Aktivität des gebildeten ^{182}Ta kann man Tantal bis in beinahe 10% an diesem Element armen Mischungen bestimmen.

2. Methode. Sie ist eine Vervollkommnung des klassischen Verfahrens der Abtrennung dieser Oxyde mit Tannin. Zu der zu bestimmenden Lösung fügt man radioaktives Niob ^{95}Nb von bekannter spezifischer Aktivität zu, dann wird Tantal mit Tannin bei pH 3.8 ausgefällt; dabei fällt ebenfalls ein Teil des Niobs aus. Das Niob wird darauf bei einem etwas höheren pH in dem Filtrat ausgefällt. Die Messung der Aktivität der zwei Fraktionen erlaubt zu bestimmen wie die Teilung sich vollzog und die nötige Korrektur einzuführen. Titan wird kolorimetrisch nach dem Glühen der in der Lösung zurückgebliebenen Oxyde bestimmt.

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COLORIMETRIC DETERMINATION OF MOLYBDENUM WITH DISODIUM-1,2-DIHYDROXYBENZENE-3,5-DISULFONATE *

by

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In articles describing the colorimetric determination of iron (III) by YOE AND JONES[7] and of titanium (IV) by YOE AND ARMSTRONG[6] with disodium-1,2-dihydroxybenzene-3,5-disulfonate (Tiron), it was observed that a yellow color is formed with molybdate ions. This suggested a possible use of Tiron for the colorimetric determination of molybdenum.

Tiron is a derivative of catechol and the color reaction between catechol and molybdenum has been reported in the literature[2, 5]. SEIFTER AND NOVIC[3] observed a yellow color produced by catechol and molybdate with a sensitivity of 4.2 p.p.m. molybdenum. SHAPIRO[4] has recently reported pyrocatechuic aldehyde as a colorimetric reagent and observed a sensitivity of 0.2 p.p.m. molybdenum.

A Note on the use of Tiron as a colorimetric reagent for molybdenum (VI) has recently been published from this laboratory[8]. In the article that follows, details of a critical study of this reagent are presented, together with its use for the determination of molybdenum in a variety of materials.

APPARATUS AND REAGENTS

Instruments. Absorbancy measurements were made with a Beckman spectrophotometer, Model DU, using 1.00-cm cells.

All pH measurements were made with a Beckman glass electrode pH meter, Model G.

Visual color comparisons were made in 50-ml Nessler cylinders (tall-form).

Tiron solution. Disodium-1,2-dihydroxybenzene-3,5-disulfonate, $C_6H_2(OH)_2(SO_3Na)_2.H_2O$, was obtained from LaMotte Chemical Products Co., Baltimore, Md., U.S.A. It is sold under the name "Tiron", proposed by YOE AND ARMSTRONG[6], because it is employed as a colorimetric reagent for both titanium and iron.

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The compound is highly soluble in water and is colorless, an advantage in colorimetric analysis. All solutions of the reagent were prepared daily, or when needed, by dissolving it in either distilled water or the potassium acid phosphate-sodium hydroxide buffer solution.

Buffer solution. A potassium acid phosphate-sodium hydroxide buffer of pH 7 was prepared by mixing 35 ml of 0.2 *N* sodium hydroxide with 50 ml of 0.2 *M* potassium acid phosphate, KH_2PO_4, and diluting to 200 ml with water.

Standard molybdenum solution. A 1000 p.p.m. molybdenum solution was prepared by dissolving 1.8401 grams of dry ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in water and diluting to a litre. The solution was standardized by precipitation of the molybdenum with α-benzoinoxime, igniting the precipitate and weighing as the oxide[1]. The 1000 p.p.m. molybdenum stock solution was diluted to any desired concentration.

Solutions of diverse ions. Reagent-grade salts were used to prepare the solutions of the various ions. The stock solutions generally contained 1 mg of the element per millilitre of solution.

α-Benzoinoxime solution. This reagent was obtained from Eastman Kodak Co., Rochester, N. Y., U.S.A. Two grams of the compound were dissolved in 100 ml of 95% ethanol.

Absorption curve of the colored complex

Confirming the observations of YOE AND JONES[7] and YOE AND ARMSTRONG[6], a bright yellow color was formed on a spot plate when one drop of a Tiron solution was added to a drop of molybdate solution. From Fig. 1, it is seen that the yellow molybdenum-Tiron complex has a maximum absorbancy at 390 mμ. This solution contained 5 p.p.m. molybdenum and 1.6% Tiron and had a pH of 7.

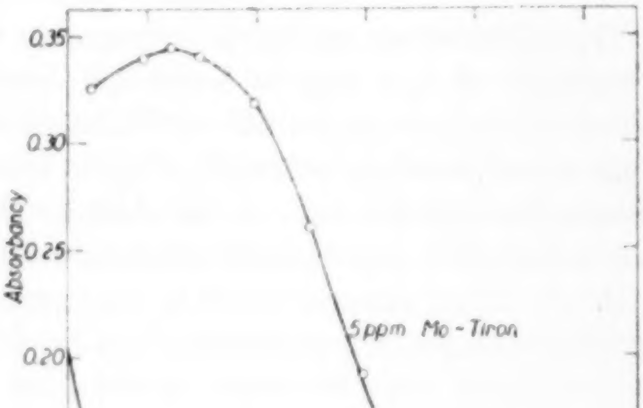

Fig. 1.

Effect of pH *on Tiron*

At high pH values, *i.e.*, 11-12, a solution of Tiron turns to a bright greenish-yellow; the intensity is dependent on the Tiron concentration. Hence, the effect of pH on the Tiron solution was investigated.

Absorbancy measurements were made with 2% Tiron solutions at various pH values and at 390 mμ against distilled water. Fig. 2 shows that the Tiron solution begins to absorb appreciably at pH 9 and increases rapidly between pH 9.5-11. Fortunately, at 390 mμ, the Tiron solution is colorless at the optimum pH 6.6-7.5 of the yellow molybdenum-Tiron complex.

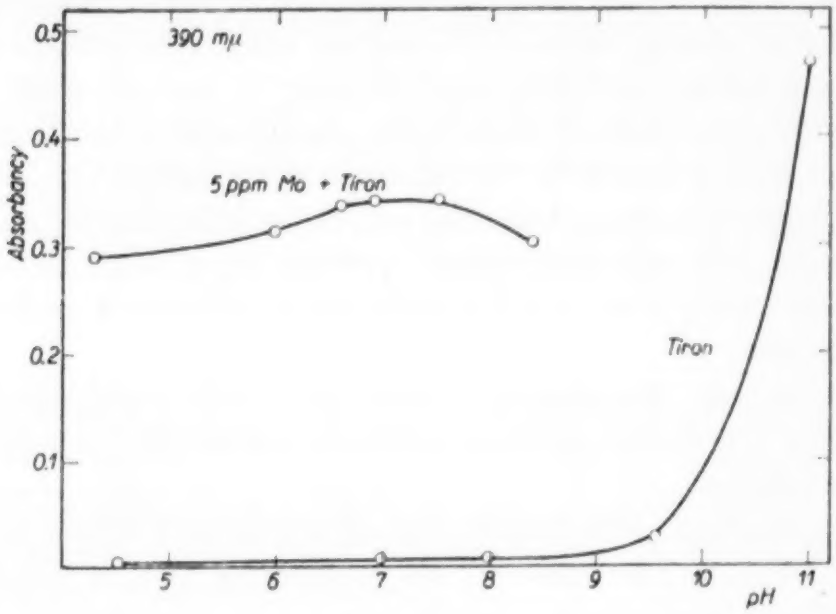

Fig. 2.

Effect of pH *on the color reaction*

The effect of pH on the color reaction was studied by taking absorbancy measurements at 390 mμ of solutions containing 5 p.p.m. molybdenum and 2% Tiron at various pH values. A "blank" was made up at the same pH values for each corresponding solution. Fig. 2 shows that the highest color intensity is obtained at pH 6.6 to 7.5; no shift in the wavelength of maximum absorbancy was noted. A 5 p.p.m. molybdenum solution was chosen because its absorbancy with 2% Tiron occurred within the optimum absorbancy range of 0.2-0.7 optical density using a 1.00-cm cell.

Tiron concentration

The effect of the Tiron concentration on the colored complex was studied by taking absorbancy measurements at 390 mμ on solutions containing 5 p.p.m. molybdenum at concentrations of 0.5%, 1.0%, 1.5%, and 2.0% Tiron, respectively. Maximum absorbancy was obtained with 1% Tiron; there was no increase in intensity at higher Tiron concentrations. A concentration of 1.5-2% Tiron was chosen in order to insure maximum color intensity over the optimum range of molybdenum concentration. For a 5 p.p.m. molybdenum and 1% Tiron solution, the mole ratio of Tiron to molybdenum is about 600 to 1, demonstrating that a very large excess of Tiron must be present for full color intensity of the complex.

References p. 557.

Buffer solution

The potassium acid phosphate-sodium hydroxide buffer of pH 7 introduced no interference and was satisfactory in stabilizing the pH of the colored complex solution.

Absorbancies of solutions containing 5 p.p.m. molybdenum and 1.6% Tiron were measured at 390 mμ, after varying amounts of the buffer were added. Two, five, and ten millilitres, respectively, of the buffer per 25 ml of solution showed no variation in the absorbancy. A volume of 5 ml per 25 ml of solution was chosen.

Order of adding the reagents

It was observed that the absorbancy was low when the constituents were added in the following order: molybdenum, Tiron, pH adjustment to 7, and buffer. However, when the pH was adjusted to 7 and the buffer added *before* the Tiron solution, the maximum absorbancy was obtained. Hence, the color must be formed at the optimum pH and not before. The order of adding the reagents is thus: molybdenum, pH adjustment to 7, buffer, and Tiron.

Sensitivity of the reaction

Fifty millilitres of the molybdenum complex containing 1.6% Tiron, 10 ml of the buffer, and 0.05 p.p.m. and 0.1 p.p.m. molybdenum, respectively, were prepared. These solutions were compared against a "blank" in both Nessler cylinders and the Beckman spectrophotometer. Only the 0.1 p.p.m. molybdenum solution was distinguishable from the "blank" in Nessler tubes; it had an absorbancy of 0.007 at 390 mμ. As a conservative value, the practical sensitivity of the color reaction was taken as 1 part of molybdenum in 10 million parts of solution, *i.e.*, 0.1 p.p.m. molybdenum.

Spot-plate sensitivity tests were carried out by transferring 0.05 ml of a standard molybdenum solution to a depression in a white porcelain spot plate, adding 0.05 ml of the buffer of pH 7, and finally 0.05 ml of an 8% Tiron solution. "Blanks" were prepared by adding buffer solutions to the reagent alone. The lowest concentration of test solution to give a color distinguishable from the "blank" was 5 p.p.m. molybdenum. Thus, 0.25 γ of molybdenum may be detected on a spot plate.

Effect of temperature on the reaction

Twenty-five millilitres of the colored complex containing 5 p.p.m. molybdenum, 1.6% Tiron, and buffer showed no change in the color intensity over a temperature range of 15° to 40° C when the absorbancies were measured at 390 mμ.

Rate of reaction and stability of the complex

The reaction between Tiron and molybdate ions is instantaneous and the color is stable for at least three weeks. The colored complex has a negligible increase in intensity over the first six hours, but the intensity remains constant thereafter. However, absorbancy measurements were taken immediately after mixing.

Beer's law

The molybdenum-Tiron complex obeys Beer's law over a concentration range of 0.2 p.p.m. to 10 p.p.m. molybdenum at 390 mμ; the practical range is 3 p.p.m. to 10 p.p.m., which gives absorbancies between 0.2-0.7 optical density.

Effect of diverse ions

Reactions with various ions. Tests were made by YOE AND JONES[7] on spot plates; 78 ions in all were tested. The following ions produced colored solutions with the reagent: Fe^{+3} (blue in acid solution, red in alkaline), MoO_4^{-2} (yellow), OsO_5^{-2} (yellow), Cu^{+2} (greenish yellow in alkaline solution), UO_2^{+2} (yellow), VO^{+2} (purple color which fades to colorless), and Ti^{+4} (intense yellow). Ag^+ and $AuCl_4^-$ are reduced to the metallic state.

Al^{+3}, Ca^{+2}, Ce^{+3}, Sn^{+4}, Zr^{+4}, Th^{+4}, Hg^{+2}, WO_4^{-2}, and Pb^{+2} appear to form colorless complexes with the reagent. However, a large excess of Tiron, used in the procedure for molybdenum, should largely overcome any interference due to these ions. As seen in Fig. 1, the tungsten-Tiron complex begins to absorb below 410 mμ. Since Fe^{+3}, OsO_5^{-2}, UO_2^{+2}, VO^{+2}, and Ti^{+4}, form colored complexes, they must be absent. The elimination of Fe^{+3} and WO_4^{-2} interference will be discussed in later sections.

Tolerance to diverse ions. Five millilitres of 25 p.p.m. molybdenum were pipetted into a 25-ml volumetric flask to which was added the diverse ion being investigated. The pH was adjusted to 7 with 0.1 *N* sodium hydroxide, then 5 ml of the buffer and 5 ml of 8% Tiron solution were added, and the solution diluted to 25 ml. The final solution contained 5 p.p.m. molybdenum and 1.6% Tiron. The pH was checked and the absorbancy measured at 390 mμ.

An ion was considered to interfere with the molybdenum color formation if the resulting solution differed by 0.005 in optical density from that containing molybdenum and no diverse ion.

Table I lists the tolerances of the diverse ions as p.p.m. of the element, unless otherwise stated. The + sign after the number means that, above the concentration listed, the ion precipitated (as the hydroxide) when the pH was adjusted to 7 with 0.1 *N* sodium hydroxide.

TABLE I

TOLERANCE TO DIVERSE IONS

Ion	Added as	Limiting concentration, p.p.m.	
Al^{+3}	$Al(NO_3)_3$	10	+
As^{+3}	$AsCl_3$	20	+
Be^{+2}	$BeCl_2$	2	+
Bi^{+3}	$Bi(NO_3)_3$	1	+
BO_3^{-3}	H_3BO_3	2	+
Ca^{+2}	$Ca(NO_3)_2$	2	+ (at 8 ppm)
Cd^{+2}	$Cd(NO_3)_2$	6	+
Ce^{+3}	$Ce(NO_3)_3$	<1	+
Ce^{+4}	$Ce(SO_4)_2$	<1	+
Co^{+2}	$Co(NO_3)_2$	6	+ (at 15 ppm)
Cr^{+3}	$Cr(NO_3)_3$	1	+
Cu^{+2}	$Cu(NO_3)_2$	1	+
Fe^{+3}	$Fe_2(SO_4)_3$	<0.3	
Hg^{+2}	$HgCl_2$	1	+ (at 20 ppm)
HPO_4^{-2}	Na_2HPO_4	100	(as HPO_4^{-2})
Mg^{+2}	$MgCl_2$	20	+
Mn^{+2}	$MnCl_2$	<1	+
Ni^{+2}	$Ni(NO_3)_2$	4	+
Pb^{+2}	$Pb(NO_3)_2$	6	+
Sb^{+3}	$SbCl_3$	10	+
SiO_3^{-2}	Na_2SiO_3	200	
Sn^{+2}	$SnCl_2$	2	+
Sn^{+4}	$SnCl_4$	2	+
Th^{+4}	$Th(NO_3)_4$	4	+
UO_2^{+2}	$UO_2(NO_3)_2$	<1	
WO_4^{-2}	Na_2WO_4	<1	
Zn^{+2}	$Zn(NO_3)_2$	10	
Zr^{+4}	$Zr(NO_3)_4$	4	+
Citrate	Citric acid	1000	
Biphthalate	Potassium biphthalate	500	

The following ions (Table II) caused no interference at the concentrations given; higher concentrations were not tested.

TABLE II

Ion	Added as	Concentration, p.p.m.
Br^-	KBr	2000
Cl^-	KCl	6000
F^-	KF	100
I^-	KI	1000
NO_3^-	KNO_3	1000 (as NO_3)
Oxalate	Oxalic acid	500
Tartrate	Tartaric acid	500

RECOMMENDED PROCEDURE FOR MOLYBDENUM

The sample weight should be chosen so that a convenient volume will contain 15 to 50 p.p.m. molybdenum. Thus, a 5-ml aliquot of this solution, diluted to 25 ml, would contain 3 to 10 p.p.m. molybdenum, the optimum concentration range.

Dissolve the sample by an appropriate method using fusion, mineral acids, or both. Remove interfering ions by the usual methods of separation. Transfer the solution containing molybdenum to a convenient size volumetric flask and dilute to the mark with water. After mixing, transfer 5 ml by means of a pipet to a 25-ml volumetric flask. Adjust the pH with a sodium hydroxide or an ammonium hydroxide solution to within the optimum pH range of 6.6 to 7.5. Add 5 ml of a potassium acid phosphate-sodium hydroxide buffer of pH 7, 5 ml of 8-10% Tiron solution made up in distilled water or preferably with the buffer solution, and dilute the mixture to 25 ml. After thorough mixing, compare the colored complex with previously prepared standards covering the range of concentration under consideration, *i.e.*, 3 to 10 p.p.m. molybdenum, at 390 mμ. If molybdenum is separated from interfering ions with α-benzoinoxime, a few millilitres of acetone should be added to the mixture before dilution to 25 ml; this prevents the precipitation of the α-benzoinoxime reagent.

SEPARATION OF MOLYBDENUM FROM INTERFERING IONS

As noted in Table I, iron must be completely absent when determining molybdenum with Tiron. Also, YOE AND JONES[7] show that the iron-Tiron complex has appreciable absorption at 390 mμ and pH 7, the wavelength and pH at which the molybdenum complex is measured.

Instead of separating the diverse ions from molybdenum, the latter may be separated from almost all other elements by precipitating it with α-benzoinoxime. This is one of the classical methods[1] for the quantitative gravimetric determination of molybdenum. Although the reagent also precipitates W, Pd, Cr(VI), V(V), and Ta, the elimination of W, Cr, and V may be accomplished readily; Pd and Ta cause no inteference.

In the procedure by KNOWLES[1] the molybdenum (VI) is precipitated by α-benzoinoxime, ignited and weighed as MoO_3. However, we use the method only as a means of separating molybdenum. Subsequently, the precipitate is dissolved and the molybdenum determined colorimetrically with Tiron, thus effecting a considerable saving in time.

The molybdenum α-benzoinoxime precipitate is readily soluble in warm dilute ammonium hydroxide. A small residue may remain undissolved; it is the excess of α-benzoinoxime reagent and contains a trace of molybdenum. The residue is soluble in acetone.

The following procedure is used for the precipitation of molybdenum with α-benzoinoxime: About 50 ml of a solution containing not more than 0.15 g molybdenum and 5% (by volume) of hydrochloric acid are chilled to 5°-10° C in an ice-water bath. Five to ten millilitres of 2 g α-benzoinoxime in 100 ml of 95% ethanol are added slowly with stirring. Five millilitres extra are added for each 0.01 g molybdenum present. A few millilitres of bromine water are added to oxidize any reduced molybdenum. Then, 1-2 ml reagent are added and the solution kept at 5°-10° C for ten to fifteen minutes with occasional stirring. The molybdenum α-benzoinoxime precipitate is filtered through Whatman No. 42 paper with gentle suction and then thoroughly washed with 100 ml of a cold solution containing 2.5 ml of reagent solution and 2.5 ml concentrated hydrochloric acid. The precipitate is dissolved directly on the filter paper with about 50 ml of hot 1.5 *N* ammonium hydroxide and finally with enough acetone to dissolve the reagent residue and prevent precipitation of the reagent in the filtrate. The dissolved precipitate is allowed to pass through the filter paper into a convenient size volumetric flask, the solution diluted to the mark and mixed. A suitable aliquot is analyzed for molybdenum according to the recommended Tiron procedure.

ELIMINATION OF TUNGSTEN INTERFERENCE

Fig. 1 shows that the tungsten-Tiron complex has appreciable absorption at 390 mμ, the maximum absorption peak for molybdenum-Tiron. It is obvious that solutions containing tungstate ions would give high results when analyzing for molybdenum with Tiron. Moreover, since tungsten is precipitated with α-benzoinoxime along with molybdenum, the tungsten interference must be eliminated. Fortunately, the tungsten-Tiron complex has no appreciable absorption at about 420 mμ; when tungsten is present, the molybdenum complex may be measured at 420 mμ, instead of at 390 mμ. Beer's law is obeyed by the molybdenum-Tiron complex at 390, 400, 410, 420, 430, and 440 mμ. Thus, the separation of molybdenum and tungsten may be made photometrically. This procedure was used in the determination of molybdenum in steels containing tungsten.

DETERMINATION OF MOLYBDENUM IN VARIOUS MATERIALS

In the following materials molybdenum was precipitated by α-benzoinoxime and determined colorimetrically with Tiron according to the recommended procedures.

Molybdate solutions. Table III summarizes the results.

TABLE III

MOLYBDATE SOLUTIONS

	Metals present p.p.m.	Mo taken mg	Mo found mg	Difference mg
(a)	—	6.25	6.19	−0.06
(b)	3100 Fe	2.50	2.50	0.00
(c)	6000 Fe	6.25	6.25	0.00
			6.19	−0.06
(d)	2000 each K, Ca	0.98	0.98	0.00
	1000 Mg		0.98	0.00
	200 each Na, Fe			
	40 each Al, Mn			
	20 each Co, Ni Zn, Cu			
(e)	same as (d)	5.00	4.80	−0.20
			4.90	−0.10
(f)	same as (d)	10.00	9.50	−0.50
			10.10	+0.10

Standard samples. The following procedure was generally used to dissolve steels: The sample was dissolved in 100 ml of 1:3 hydrochloric acid by heating until no further action was visible. The hydrochloric acid concentration may vary so as to give a 5% (by volume) hydrochloric acid solution when precipitating molybdenum with α-benzoinoxime. The hot solution was treated with nitric acid (1 ml will suffice for a 1 g sample) to oxidize the molybdenum and decompose the carbides. The solution was boiled to expel oxides of nitrogen and then diluted to a convenient volume in a volumetric flask. Aliquots were taken, the molybdenum precipitated with α-benzoinoxime and treated with Tiron as previously described. Variations in the procedure are given for materials of different composition.

Chromium and vanadium steels. Whenever Cr(VI) and V(V) are present in the solution, about 2 g of ferrous ammonium sulfate should be added before the addition of α-benzoinoxime. The chromium and vanadium are thus reduced to Cr(III) and V(IV), respectively, and not precipitated[1].

For high chromium steel any acid insoluble matter was filtered off and fused with sodium carbonate in a platinum crucible to recover any molybdenum. The fused mass was dissolved in hydrochloric acid and the solution added to the main filtrate.

Tungsten steels. When tungsten steels are dissolved in acid, much tungstic acid remains insoluble. If this precipitate is filtered off and the molybdenum determined in the filtrate, low values are obtained. This is due to coprecipitation of molybdenum with the tungstic acid precipitate.

Tungstic acid is soluble in 1.5 *N* ammonium hydroxide. If this alkaline solution is acidified, the tungstic acid reprecipitates and would occlude some molybdenum in the original filtrate. Hence, a separate analysis on the alkaline solution of the tungsten residue was made for molybdenum according to the recommended Tiron procedure. Absorbancy measurements were made at 420 mμ to eliminate any tungsten interference. This molybdenum value was added to the one obtained from the main filtrate.

Calcium molybdate. Dissolve the sample by heating with 25 ml of 2:1 hydrochloric acid, cool and add 20 ml of 1:1 sulfuric acid. Evaporate the solution to fumes of sulfuric acid, cool, dilute with 60 ml of water and heat gently for 10 to 15 minutes. Filter off the insoluble matter and wash with hot water. The molybdenum in the insoluble silica is recovered by ignition at 500° C, sulfuric acid-hydrofluoric acid treatment, and sodium carbonate fusion. It is not necessary to make an α-benzoinoxime precipitation on this sample.

Table IV summarizes the results for the standard samples.

TABLE IV

NATIONAL BUREAU OF STANDARDS (U.S.A.) SAMPLES

N.B.S. Sample	% Mo N.B.S.	% Mo found	Difference %
Mn metal 67	0.015	0.013	−0.002
		0.013	−0.002
Steel 19c	0.016	0.017	+0.001
		0.020	+0.004
Steel 72a	0.202	0.185	−0.017
		0.187	−0.015
		0.182	−0.020
		0.193	−0.009
Steel 133	0.559	0.540	−0.019
		0.549	−0.010
Steel 36	1.01	1.01	0.00
		1.01	0.00
Steel 160	2.95	2.92	−0.02
		2.90	−0.05
		2.94	−0.01
		2.87	−0.08
		2.92	−0.03
		2.87	−0.08
		2.95	0.00
		2.92	−0.03
		2.94	−0.01
		2.92	−0.03

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N.B.S. Sample	% Mo N.B.S.	% Mo found	Difference %
Steel 132	7.07	6.41	−0.66
(6% W)		6.91	−0.16
		6.91	−0.16
		7.01	−0.06
Steel 134	8.68	8.69	+0.01
		8.30	−0.38
(1.5% W)		8.51	−0.17
CaMoO$_4$ 71	35.3	35.4	+0.1
		35.6	+0.3

SUMMARY

A procedure for the colorimetric determination of molybdenum with disodium-1,2-dihydroxybenzene-3,5-disulfonate (Tiron) has been presented. The maximum absorbancy of the yellow colored complex is at 390 mμ; the optimum pH range is 6.6-7.5; and the Tiron concentration is 1.5-2%.

The color reaction conforms to Beer's law and has a practical sensitivity of 0.1 p.p.m. molybdenum. The color formation is instantaneous and stable for at least three weeks. There is no temperature effect over the range of 15°—40° C.

The tolerances of the colored complex to many diverse ions have been established. The separation of molybdenum from interfering ions is accomplished by precipitation of the former with *α*-benzoinoxime. Molybdenum and tungsten are separated photometrically.

The colorimetric determination of molybdenum with Tiron was successfully applied to a variety of steels and other materials.

RÉSUMÉ

Une méthode de dosage colorimétrique du molybdène, au moyen de disulfonate de disodium-1-2-dihydroxybenzène-3-5 (tiron), est proposée. L'absorption maximum de la coloration jaune du complexe formé est à 390 mμ; intervalle de pH: 6.6 à 7.5; concentration du tiron 1.5 à 2%. La coloration obéit à la loi de Beer et la sensibilité de cette réaction est de 0.1 p.p.m. de molybdène. La formation de la coloration est instantanée et stable pendant 3 semaines au moins. Des variations de températures de 15 à 40° C sont sans effet. D'autre part l'influence de divers ions sur ce complexe a été étudiée. On sépare le molybdène des ions gênants par précipitation avec l'*α*-benzoïnoxime. Le molybdène et le tungstène sont séparés par photométrie. Ce dosage colorimétrique du molybdène au moyen de tiron a été appliqué avec succès pour des analyses d'aciers et autres substances.

ZUSAMMENFASSUNG

Ein Verfahren zur kolorimetrischen Bestimmung von Molybdän mit dem Dinatriumsalz der 1.2-Dioxybenzen-3.5-disulfonsäure (Tiron) wurde vorgestellt. Das Absorptionsmaximum des gelb gefärbten Komplexes liegt bei 390 mμ, der optimale pH-Bereich bei 6.6-7.5 und die Tironkonzentration 1.5-2%.

Die Farbreaktion erfüllt das Beer'sche Gesetz und hat eine praktische Empfindlichkeit von 0.1 Teilen Mo/10^6. Die Farbbildung erfolgt augenblicklich und ist mindestens 3 Wochen haltbar. In dem Bereich von 15-40° C ist kein Temperatureinfluss bemerkbar.

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Der Einfluss der verschiedenen Ionen auf den Farbkomplex wurde festgestellt. Die Abtrennung des Molybdäns von störenden Ionen wurde durch die Ausfällung des ersteren mit α-Benzoinoxim erreicht. Molbdän und Wolfram werden photometrisch abgetrennt.

Die kolorimetrische Bestimmung des Molybdäns mit Tiron wird mit Erfolg auf eine Anzahl von Stählen und andere Stoffe angewandt.

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THE POLAROGRAPHIC BEHAVIOUR OF SOME ELEMENTS IN CONCENTRATED CALCIUM CHLORIDE SOLUTION

I. GENERAL INTRODUCTION. CERTAIN PROBLEMS ARISING FROM THE USE OF 5*M* CALCIUM CHLORIDE.

by

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GENERAL INTRODUCTION

The investigation outlined in this and subsequent papers was undertaken with the object of developing a polarographic method for the determination of a number of elements present in trace quantities as impurities in calcium metal.

A search of the literature revealed that, apart from a relatively insensitive method for chromium[1], no polarographic methods for the determination of impurities in calcium were reported. There are, however, a large number of methods for the determination of elements in aluminium, magnesium and light alloys[2, 3], although these were considered to be too insensitive to be adapted for use with calcium. The general procedure adopted in these methods involves the dissolution of the metal in acid and suitable adjustment of the pH followed by polarography.

In view of the fact that it was required to determine impurities of the order of parts per million it was necessary either to employ chemical concentration procedures, or to use a much more concentrated solution of the base electrolyte (calcium salt) than is normally employed. It was considered that the former alternative would entail very complicated chemical separations for each element and offer no advantage over those methods at present in use. We therefore decided to adopt the latter procedure and carry out the determination in a very concentrated calcium chloride solution.

5 molar calcium chloride was selected as the base electrolyte as this is sufficiently below saturation point for use in routine work while providing an adequate concentration of the impurities in the final solution. Under these conditions an impurity present to the extent of 10 parts per million in the original metal would yield a concentration of 2 μg per ml in the final solution. However, the use of such a concentrated base electrolyte leads to two types of difficulties. The first type is due to the high viscosity of such a solution and the second to its high ionic strength and low water free energy. The latter leads to unexpected polarographic behaviour on the part of some elements, a subject which will be treated fully in parts II and III of this series.

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The investigation was confined to the elements copper, chromium, nickel, lead, cadmium, iron and manganese. All others were rejected either because they were not polarographically reducible, or because their half-wave potentials were too close to that of calcium, or because they were likely to be present in such small amounts that they would not be detectable even under the conditions adopted.

The majority of the work was carried out using the Randles type single sweep cathode ray polarograph developed in this Department[4, 5]. This instrument is much more sensitive than conventional instruments and is much speedier in operation. The characteristic reduction potential measured on this instrument is that of the peak of the wave, but for the purpose of discussion all such potentials have been converted to half-wave potentials by subtraction of 0.05 volts [5]. The term "diffusion current" when referring to cathode ray polarograms will be the current flowing at the peak of the wave.

Except where otherwise stated all potentials are given versus the normal hydrogen electrode (vs. N.H.E.) and the American sign convention has been employed. On this convention the saturated calomel electrode (S.C.E.) which was used as the standard half-cell for the measurement of potentials, was assumed to be —0.245 volts vs. N.H.E. No corrections for liquid junction potentials have been attempted.

The half-wave potentials and suitable pH ranges for the polarography of each element examined have been calculated in each case by means of the usual equations[6]. They are compared with the practical results in the later papers and discrepancies, where they occur, are explained.

The potential of the mercury pool (which was used as the anode for much of the work) was found to be —0.186 volts vs. N.H.E. when in contact with $5M$ calcium chloride solution. This agrees well with the calculated value of —0.195 volts.

CERTAIN PROBLEMS ARISING FROM THE USE OF $5M$ CALCIUM CHLORIDE

Preparation of solutions of standard acidity

For the fundamental investigational work a solution prepared from calcium carbonate was used. The following procedure was employed. Calcium carbonate was dissolved in the minimum amount of hydrochloric acid and diluted to give a $2.5M$ calcium chloride solution. 20 ml aliquots of this were evaporated until a crust just formed on the surface of the solution. Water and sufficient hydrochloric acid or sodium hydroxide to give the required pH were then added so that the final volume was 10 ml, and this solution was polarographed. Elements to be studied were added to the aliquots of $2.5M$ calcium solution before evaporation. Nitric acid was not used for the dissolution since the presence of nitrate ion at the dropping mercury electrode would interfere with the determination

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of some elements. It is essential that the amount of hydrochloric acid used be carefully controlled. If too much is added initially and the excess is removed by evaporation to dryness, some of the elements present as impurities or by addition are rendered insoluble in the final solution. By using the treatment outlined above, however, and making a standard addition of acid or alkali, solutions having a desired pH to within ± 0.75 units can be prepared, even in the range 6-8. Complete experimental details of the above method, together with those of the method for the preparation of solutions from samples of calcium metal will be given in part IV of this series.

pH *measurement and control*

The measurement of the pH of a $5M$ calcium chloride solution was found to be impossible. The meter readings were unsteady and successive readings using the same solution gave widely differing results. The difficulty was overcome by diluting the solution tenfold. This procedure does not enable the absolute value of the pH of the $5M$ solution to be determined, but comparisons can quickly and easily be made. Also, if the hydrogen ion activity coefficient in $0.5M$ calcium chloride solution is assumed to be unity, whilst that in the $5M$ solution is at least four[7], then the maximum pH of the concentrated solution will be: —

$$\text{maximum pH}_{(\text{conc.})} = \text{measured pH}_{(\text{dil.})} - 0.4$$

All pH values quoted in these papers will refer to those of the tenfold diluted solution.

Due to the uncertain value of the hydrogen ion activity theoretical amounts of acid or alkali to give a desired pH to the $5M$ calcium solution could not be calculated. Graphs showing the change in pH of the solution with addition of standard acid or alkali solutions were therefore prepared. A typical graph is shown in Fig. 1.

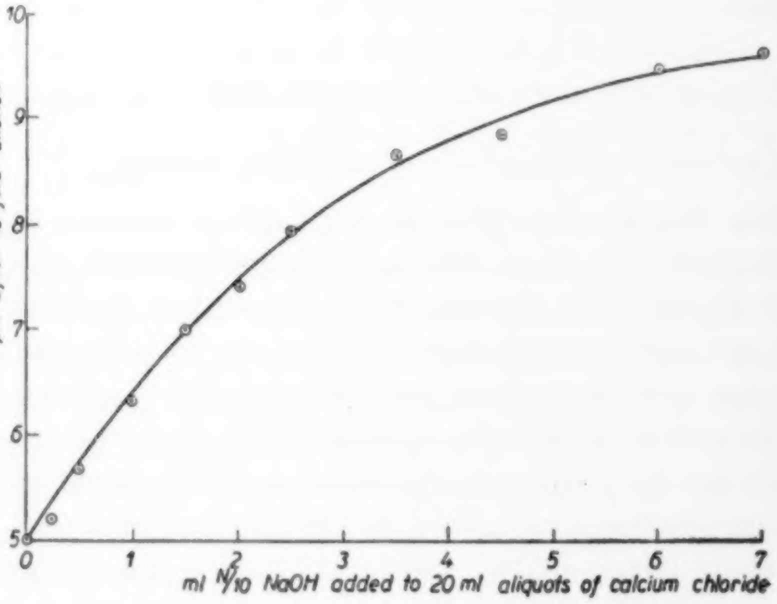

Fig. 1. Effect of NaOH on the pH of calcium chloride.

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General polarographic behaviour

Solutions of copper, chromium, nickel, lead, cadmium and manganese in $5M$ calcium chloride solution, prepared as described above, were examined using both a Cambridge photographic-recording polarograph and the linear sweep cathode-ray polarograph mentioned earlier. The pH values of these solutions were adjusted so that the element under examination was fully in solution in an ionic form. The diffusion currents obtained using the conventional polarograph were found to be only about one-half of the values calculated by means of the Ilkovic equation. Those obtained using the cathode-ray polarograph were between one-half and one-sixth of the values calculated using the simplified Randles equation[4, 5]. For the purposes of these calculations the diffusion coefficients employed were those pertaining to dilute solutions and clearly this data cannot apply to polarography in a medium of such high viscosity as $5M$ calcium chloride. BRASHER AND JONES[8] have pointed out that little attention has been paid to the effects of viscosity on polarography and have indicated the inadvisability of neglecting these effects in quantitative work. The diffusion coefficient or large, uncharged, spherical molecules is known to be inversely proportional to the viscosity of the medium and this correction has been successfully applied to the diffusion coefficients of many of the small charged ions normally involved in polarographic reductions[8, 9].

The relative viscosity of $5M$ calcium chloride solution with respect to water, measured using an Ostwald viscometer, was 4.85 at 25° C. The calculated diffusion currents mentioned above were accordingly corrected by a factor of $(1/4.85)^{\frac{1}{2}}$ when the values obtained by means of the Ilkovic equation agreed well with those found experimentally using the Cambridge polarograph. The diffusion currents measured using the cathode ray polarograph, however, were still generally lower than the calculated values, *viz.*: lead 100%, cadmium 95%, copper 85%, manganese 80%, chromium 70% and nickel 35%.

This phenomenon of low recoveries was noted by RANDLES[4] who ascribed it to irreversibility and to the rate of the electrode reaction. The effect has also been studied by DELAHAY[10] using a multi-sweep cathode ray polarograph, which, unlike our apparatus, applies the total potential change a number of times in the lifetime of one mercury drop. He concluded[11] that where the results obtained by the single-sweep and multi-sweep methods are similar, but lower than those predicted theoretically, the discrepancy is mainly due to the irreversibility of the cathodic process. If the single-sweep method gives approximately the correct result, while the multi-sweep technique gives results which only approach the theoretical value at relatively low rates of change of potential, the discrepancy is due to the slow rate of the electrode reaction. It appears, however, that these suggestions may have to be modified in view of our results, and his later findings that capacity effects distort the waves and that, in the quiescent periods between the application of successive potential sweeps the depletion of the reducible ion around the drop is not made good, and oxidation of the reduced species occurs[11]. For this reason, our comparison of the results obtained by the two methods, given below, should be treated with reserve, as those obtained by the multi-sweep technique were reported before these inherent disadvantages were realised.

DELAHAY, using a rate of change of potential of the order of 10 volts per second, has reported recoveries of 82, 70 and 17 per cent. for cadmium, lead and nickel respectively[10]. Our recoveries, using a sweep rate of 0.3 volts per second are, respectively, 95, 100 and 35 per cent. We conclude that lead is reversibly, and cadmium, slightly irreversibly, reduced at the dropping mercury electrode. The reduction of nickel is anomalous and it appears that the discrepancies may be associated with the kinetics rather than the reversibility of the electrode reaction. This will be discussed in detail in Part II of this series. The fact that the recoveries reported by DELAHAY are considerably lower than those found by us may be accounted for by an insufficient rapidity of the electrode reaction in each case, but it may also be due, either wholly or partly, to the factors related to the rapidly repeated potential sweep, which have been mentioned above.

Further information regarding the real nature of many of the reductions at present considered to be reversible should become available when the use of the cathode ray technique becomes more general, especially when a single-sweep instrument having a variable rate of change of potential is constructed. Due to the complexity of the derivation of the Randles equation, further analysis of a more quantitative nature is difficult and has not been attempted. Until such a treatment is made, the percentage of the calculated diffusion current obtained in practice may be taken as some measure of the "non-ideal" behaviour of the ionic species being reduced at the dropping mercury electrode of the cathode-ray instrument. The remarks made above serve to emphasise that in all work of this type it is essential to quote the rate of change of potential employed, in order to facilitate future comparisons.

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SUMMARY

Certain problems associated with the polarography of metals in $5M$ calcium chloride solution and the acidity control of this base electrolyte are discussed. The general results obtained by the use of a single-sweep cathode ray polarograph are given and suggestions regarding the fundamental nature of some electrode reactions are made.

References p. 563.

RÉSUMÉ

Certains problèmes, en relation avec la polarographie des métaux, en solution dans le chlorure de calcium 5*M*, et le contrôle de l'acidité de cet électrolyte de base, sont discutés. Les résultats généraux obtenus avec l'oscilloscope à rayon cathodique („single-sweep") sont donnés et des suggestions sont faites concernant la nature de quelques réactions aux électrodes.

ZUSAMMENFASSUNG

Gewisse Probleme, die mit der Polarographie von Metallen in 5*M* Calciumchloridlösung und der Kontrolle der Säurestärke dieser basischen Elektrolyte verbunden sind, werden besprochen. Die erhaltenen allgemeinen Ergebnisse bei der Benützung eines „single sweep" Kathodenstrahlpolarographen werden gegeben und Vermutungen bezüglich der fundamentalen Natur einiger Elektrodenreaktionen werden besprochen.

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THE POLAROGRAPHIC BEHAVIOUR OF SOME ELEMENTS IN CONCENTRATED CALCIUM CHLORIDE SOLUTION

II. THE POLAROGRAPHY OF CHROMIUM, NICKEL AND LEAD

by

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INTRODUCTION

This paper discusses in detail the polarographic behaviour of Cr(III), Ni(II), and Pb(II) in $5M$ calcium chloride solution. The reasons for such a study in this base electrolyte, and one method for its preparation, have already been given in a previous paper[1], in which the general difficulties inherent in the use of a medium of such high viscosity and low water free energy have also been described.

The work was carried out on a Randles type single sweep cathode ray polarograph constructed in these laboratories[2, 3] as this instrument is much more sensitive than conventional instruments and is much more rapid in operation. The essential differences between the results obtained by cathode ray methods and those of conventional polarography have already been discussed[1, 3].

All potentials quoted in this paper are true half-wave potentials versus the normal hydrogen electrode (vs. N.H.E.) and the American sign convention has also been employed throughout. All pH values refer to solutions which have been diluted tenfold since, as already stated[1], direct pH determinations on $5M$ calcium chloride are almost meaningless.

THE POLAROGRAPHY OF CHROMIUM

The possible electrochemical reductions of chromium are: —

Cr(VI) → Cr(III) . . . . a.
Cr(III) → Cr(II) . . . . b.
Cr(II) → Cr . . . . c.

A solution containing chromate ions may, therefore, give three steps when reduced at the dropping mercury electrode. In practice a fourth step is actually found, which is said to be due to an incomplete Cr(VI) → Cr(III) reduction[4]. Reduction (a) is usually recommended for the polarographic determination of chromium, employing $0.1N$ sodium hydroxide as the base electrolyte, but the criteria, laid down in the previous paper[1], for the development of a method for the determination of impurities in calcium metal (particularly the desirability of determining several elements in the same solution) were not compatible with this and the reduction was therefore not investigated.

The reduction (b) had not been comprehensively studied until recently and is usually considered less satisfactory for the determination of chromium. The remaining reduction (c) is unsatisfactory, due to the simultaneous discharge of hydrogen ion[5]. Our investigations were therefore confined to the Cr(III) → Cr(II) reduction.

The reversible potential for the reduction: —

$$Cr^{+2} \rightarrow Cr^{+3} + e^-$$

was calculated to be + 0.18 volts (vs. N.H.E.) in 5*M* calcium chloride. However some overvoltage is to be expected, due to the hydration of the Cr^{+3} ion.

The half-wave potential of this reduction has been reported to be + 0.67 volts vs. N.H.E.[6, 7] in 0.1*M* potassium chloride, but in this medium we have usually found a composite wave consisting of two steps very close to each other, having half-wave potentials of approximately + 0.63 and + 0.81 volts. WILLIS[8] has reported that the half-wave potential of the violet species of chromium $[Cr(H_2O)_6]^{+3}$ in 1*N* potassium sulphate is + 0.796 volts, whilst that of the green species (probably $[Cr(H_2O)_4SO_4]^+$) is 1.013 volts in the same medium. HAMM AND SCHULL[9] have recently shown that a freshly prepared Cr(III) solution in 0.4*M* potassium chloride gives, on reduction at the dropping mercury electrode, one step at + 0.365 volts. When this solution was allowed to age they observed a second step having a half-wave potential of + 0.64 volts. The step height of the latter increased with time whilst that of the former (at 0.365 volts) underwent a corresponding decrease in height. PECSOK AND LINGANE[10] have reported a half-wave potential + 0.27 volts for Cr(III) in saturated calcium chloride.

We prepared a saturated Cr(III) solution by reducing slightly acid potassium dichromate with hydrogen peroxide and this solution was then allowed to stand for several weeks before use. 5*M* calcium chloride solutions containing aliquots of this solution were prepared and polarographed. Two reduction steps were obtained, the first at + 0.32 volts and the second at + 0.61 volts. On heating the solutions the second step decreased in height, while the first step underwent an increase, until after heating to 100° C, only one step at + 0.32 volts remained. No alteration in the height of this step was found after the heated solutions had been allowed to stand for periods up to one week. On diluting, however, the wave at + 0.61 volts re-appeared.

It appears from the foregoing that three different species of Cr(III) ions are reducible at the dropping mercury electrode in chloride solution, at potentials of approximately + 0.32, + 0.62 and + 0.80 volts. WILLIS attributed the wave at 0.80 volts in sulphate solution to the reduction of the $[Cr(H_2O)_6]^{+3}$ ion. HAMM AND SCHULL, however, attributed their first wave (at + 0.365 volts) to the reduction of either $[CrCl_2(H_2O)_4]^+$ or $[CrCl(H_2O)_5]^{+2}$ and the second wave (at + 0.64 volts) to the reduction of $[Cr(H_2O)_6]^{+3}$. They studied the rate of transition and found it dependent on the Cr(III) and hydrogen ion concentration, and on temperature, but independent of the chloride concentration and of the ionic strength of the solution. While this may be so when dilute solutions are being considered, the phenomenon in concentrated calcium chloride is a function of the ionic strength. This is due, almost certainly, to the immobilisation of water molecules by co-ordination with Ca^{+2} ions. The formation of the species first reduced is thereby greatly accelerated and, once formed, it is stabilised. Furthermore the fact that we have obtained a wave for Cr(III) at + 0.81 volts in 0.1*M* potassium chloride throws doubt on their suggestions regarding the nature of the molecular species being reduced at + 0.32 and + 0.64 volts. It seems likely that the wave at + 0.81 volts is due to $[Cr(H_2O)_6]^{+3}$ and that the earlier and more reversible waves are both due to chloride-water-chromic complexes. It is interesting to note at this point that the results of WILLIS show that the sulphate-water-chromic complexes are more stable than $[Cr(H_2O)_6]^{+3}$, as they are reduced at more positive potentials (American convention).

It is obvious that when Cr(III) is to be determined polarographically it must be present in only one of the possible reducible species and this species must not change with time. Procedures which ensure this may have been employed in previous work without realising their significance, but we have not so far been able to obtain a stable species at will, except in concentrated chloride solutions.

Due to the low reduction potential of Cr(III) in 5*M* calcium chloride solution, no interference due to discharge of hydrogen ion will be encountered in acid solutions, but in alkaline solutions $Cr(OH)_3$ will precipitate. The pH at which 5 per cent. of $2 \cdot 10^{-4}$*M* Cr(III) in 5*M* calcium chloride will precipitate was calculated to be 5.2. The upper pH limit found in practice was well below this value *viz.* 3.7. This discrepancy is probably due to the fact that the calcium solutions employed invariably contained some iron which would act as a coprecipitant.

It may be seen from the above that in solutions of calcium chloride more concentrated than 3*M* and a pH value below 3.5 a stable Cr(III) species can be obtained by first heating to 100° C. Calcium chloride forms a very suitable medium for the determination of chromic chromium with no uncertainty concerning the half-wave potential. Interference is, however, encountered when nickel or lead is present and this interference will be discussed in detail later.

THE POLAROGRAPHY OF NICKEL

The only electrochemical reduction of nickel which can occur is: —

$$Ni \rightarrow Ni^{+2} + 2\ e^-$$

The thermodynamically calculated half-wave potential is $5M$ calcium chloride, assuming the reduction is reversible, is + 0.31 volts, but there is usually an overvoltage due to hydration of the Ni^{+2} ion.

It is known[11] that a high chloride concentration in the base electrolyte will reduce this overvoltage and this is due, it is stated, to the formation of complex nickelous chlorides, which, apparently, are reduced more reversibly than the hexaquo nickel ion. This has been confirmed by us in so far as the half-wave potential of the step due to nickel in $5M$ calcium chloride was found to be + 0.32 volts compared with + 0.86 volts in $0.1M$ potassium chloride. Additional evidence has been provided by Khlopin[12] who reported a value of + 0.62 volts for the reduction of nickel in 30 per cent. calcium chloride which is intermediate in chloride concentration between the previously quoted base electrolytes.

The above results indicate that there is very little overvoltage to the reduction of nickel in very concentrated calcium chloride solutions. It would therefore be expected that the diffusion current measured on a single-sweep cathode ray polarograph would approach the value calculated by means of the Randles equation[1]. This is not the case, and the fact that the value obtained in practice is much lower than the calculated value still requires explanation. If this is assumed to be due to thermodynamic irreversibility the measured value of the half-wave potential (+ 0.32 volts) should be greater than the true reversible potential. As the difference is negligible it is probable that the discrepancy between measured and calculated diffusion currents is some function of the kinetics of the primary electrode reaction. This reduction therefore appears to be the first reported case of an apparently almost reversible electrode reaction, which gives a diffusion current of a much lower order than the theoretical value on a single-sweep cathode ray polarograph. If substantiated, the general conclusions regarding electrode reactions drawn by Delahay from comparisons of the results obtained by single-sweep and multi-sweep instruments must be modified. This modification has been rendered necessary because it has hitherto been assumed that all reversible electrode reactions would occur fast enough for the diffusion current obtained by single-sweep methods to be almost the same value as that calculated theoretically.

The discharge of hydrogen ion cannot interfere with the determination of nickel and the maximum pH permissible for the quantitative estimation of this metal is governed only by the tendency for the precipitation of nickel hydroxide. Using Britton's value of $K = 8.7 \cdot 1.10^{-19}$ [13] for the reaction: —

$$Ni(OH)_2 \rightarrow Ni^{+2} + 2\ OH^-$$

the pH at which 5 per cent. of $2 \cdot 10^{-4}M$ nickel in $5M$ calcium chloride should be precipitated is calculated to be 7.3, which is in agreement with our observations.

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THE POLAROGRAPHY OF LEAD

The only electrochemical reduction of lead which can occur is: —

$$Pb(II) \rightarrow Pb$$

and the thermodynamically calculated half-wave potential for this reduction in $5M$ calcium chloride is + 0.13 volts if Pb^{+2} is the species reducing and + 0.2 volts if $PbCl^{+}$ reduces. The half-wave potential was found experimentally to be + 0.29 volts. KHLOPIN[12] has reported a value of + 0.24 volts for lead in "30 per cent. calcium chloride". In view of the known strict reversibility of this reduction, a lead species containing more chloride than $PbCl^{+}$ (*i.e.* some proportion of $PbCl_2$ molecules) is presumably reducing.

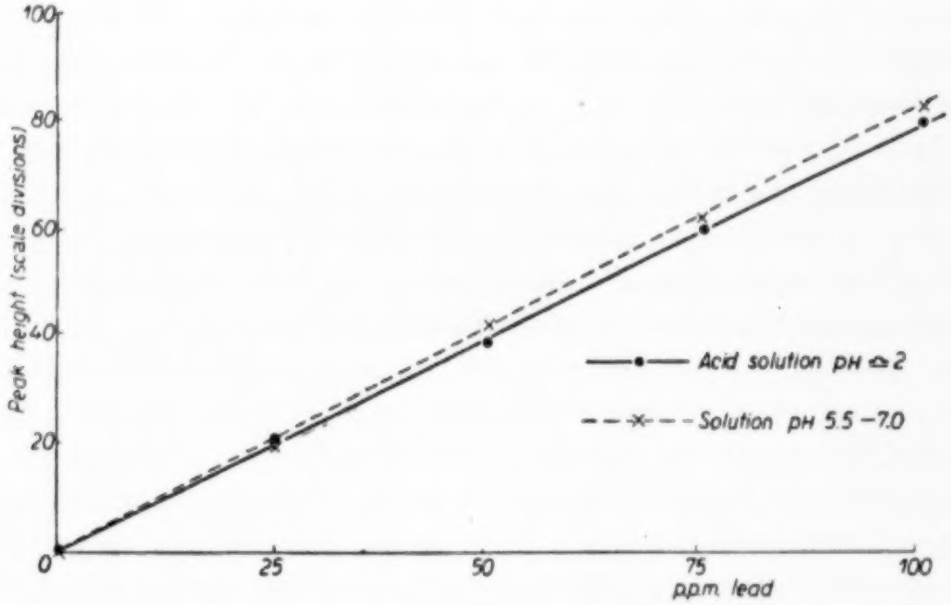

Fig. 1. Effect of pH on the lead calibration

The diffusion current due to lead increases slightly as the pH rises from 1 to 7.5. This is presumably due to a slight change in the diffusion coefficient of the ion and it causes a sufficiently large change in step height to render a calibration desirable when extreme ranges of pH values are employed. An example of two calibrations, carried out on different pH values, is shown in Fig. 1.

THE MUTUAL INTERFERENCE OF CHROMIUM, NICKEL AND LEAD

The determination of any one of these elements in the presence of the others is difficult, as the reduction steps overlap, but the wave heights are perfectly additive. If the concentrations of any two are known the third may therefore be obtained by subtraction. The variation in shape of the waves due to chromium and nickel respectively, brought about by the presence of various concentrations of the other, was studied using solutions $5M$ in calcium chloride and pH 1-2. Typical waves are given in Figs. 2 and 3, and indicate that, in spite of the fact that the number of electrons taking part in the reduction are different, the same concentration of chromium (1 electron change) and nickel (2 electron change) give similar step height. The recoveries of nickel in the presence of chromium and of chronium in the presence of nickel are given in Tables I and II.

If the pH of a solution containing chromium, nickel and lead is increased the chromium and nickel are precipitated as hydroxides. At a pH of approximately 7 only the lead remains, this providing a means of determining lead in the presence of these two interfering elements.

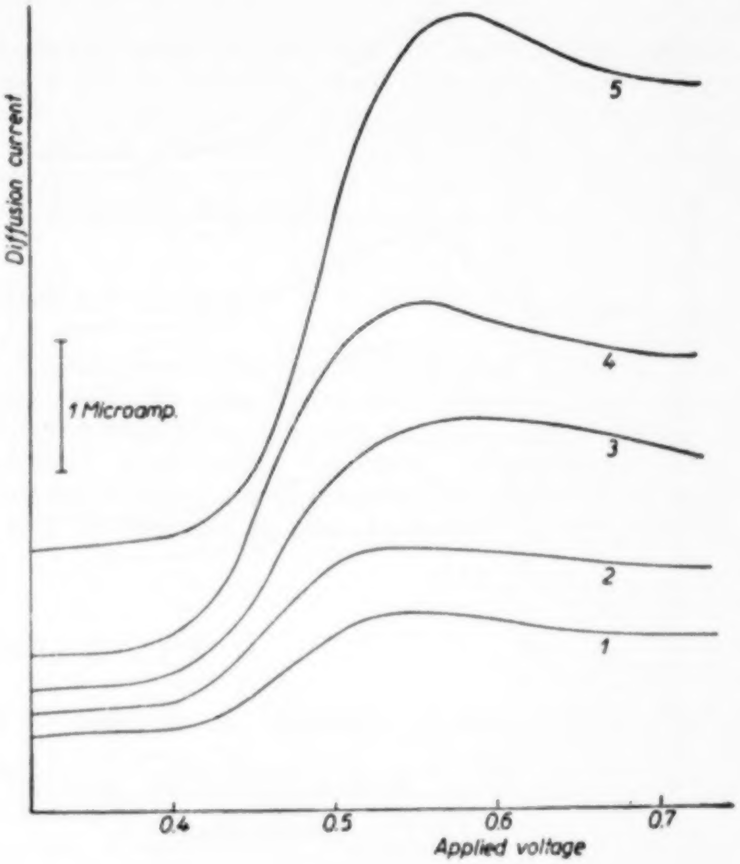

Fig. 2. Effect of nickel on the chromium wave 50 ppm chromium in the presence of:

1	25 ppm nickel
2	50 ppm ,,
3	100 ppm ,,
4	150 ppm ,,
5	250 ppm ,,

No rapid and reliable method of determining the chromium and nickel in one solution could be devised. Using two solutions, one containing the chromium as Cr(VI) and the other in the form of Cr(III) a method is possible, but the oxidation of chromium to the hexavalent state and the subsequent pH adjustment were found to be too lengthy and to require long experience before satisfactory

TABLE I

Nickel added	Nickel found	
	In absence of chromium	In presence of 25 p.p.m. chromium
5 p.p.m.	4.9 p.p.m.	— p.p.m.
10 ,,	10.2 ,,	9.5 ,,
15 ,,	15.6 ,,	— ,,
25 ,,	24.4 ,,	25.7 ,,
50 ,,	46.0 ,,	50.0 ,,

results could be obtained. Such a procedure was not considered desirable for routine work. We therefore recommend that either the chromium or nickel should be determined by a separate method (preferably chemical). Further details of this will be given in Part IV of this series.

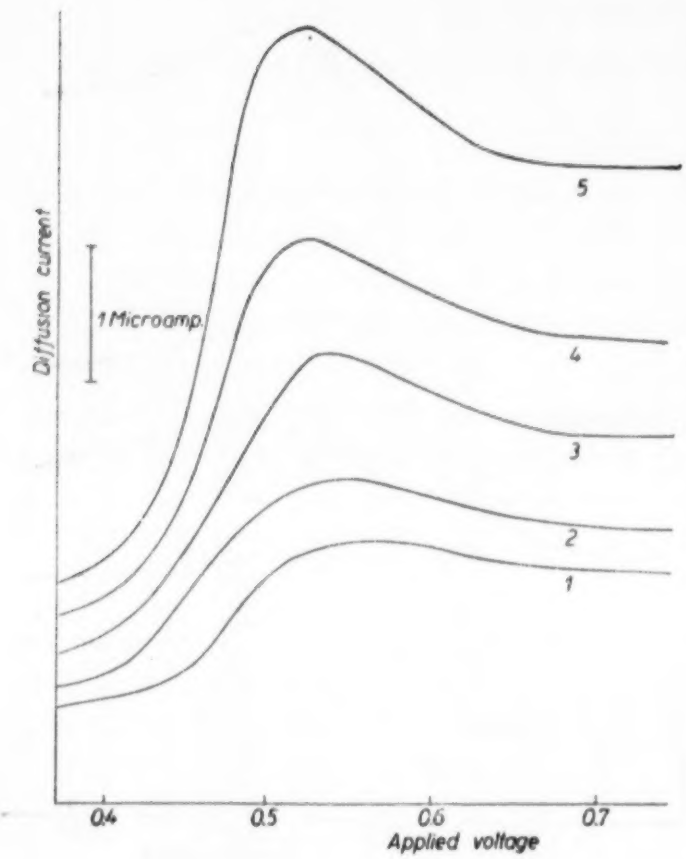

Fig. 3. Effect of chromium on the nickel wave
50 ppm nickel in the presence of:
1 25 ppm chromium
2 50 ppm ,,
3 100 ppm ,,
4 150 ppm ,,
5 250 ppm ,,

TABLE II

Chromium	Chromium found	
added	In absence of nickel	In presence of 25 p.p.m. nickel
5 p.p.m.	4.5 p.p.m.	4.8 p.p.m.
10 ,,	9.6 ,,	9.9 ,,
15 ,,	15.1 ,,	16.0 ,,
25 ,,	27.3 ,,	24.4 ,,
50 ,,	53.0 ,,	51.0 ,,

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Acknowledgement is made to the Chief Scientist, British Ministry of Supply for permission to publish this paper. The authors wish to thank Dr. J. D. H. Strickland for his advice during the work.

SUMMARY

This paper discusses in detail the polarography of chromium, nickel and lead in 5M calcium chloride. The conditions for polarography are laid down and the theoretical aspects of the results obtained with a single-sweep cathode ray polarograph are discussed. The mutual interference of the elements is detailed and recommendations for their determination in the presence of one another are presented.

References p. 571.

RÉSUMÉ

Les auteurs exposent en détail la polarographie du chrome, du nickel et du plomb avec, comme solution de base, le chlorure de calcium 5*M*. Les conditions de la méthode polarographique sont données, ainsi qu'une explication théorique des résultats obtenus avec l'oscilloscope à rayon cathodique (,,single-sweep"). Ils examinent également l'influence des éléments entre eux et ils donnent des précisions pour effectuer leur dosage les uns en présence des autres.

ZUSAMMENFASSUNG

In dieser Arbeit wird die Polarographie von Chrom, Nickel und Blei in 5*M* Calciumchlorid eingehend besprochen. Die Bedingungen für die Polarographie werden festgelegt und die theoretischen Aussichten der mit einem ,,single-sweep"-Kathodenstrahlpolarographen erhaltenen Ergebnisse werden besprochen. Die gegenseitige Störung der Elemente untereinander wird eingehend beschrieben und Vorschriften zu ihrer Bestimmung bei Anwesenheit der anderen Ionen werden gegeben.

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ÉTUDE POLAROGRAPHIQUE DE LA SALIVE

par

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Dans un travail précédent[1], nous avons entrepris l'étude qualitative du comportement de la salive au polarographe, en présence d'une solution de chlorure de cobalt (II) et d'un tampon constitué de chlorure d'ammonium et d'ammoniaque. Nous avons montré que, dans ces conditions, la salive donnait des courbes potentiel-courant très semblables à celles du sang. On y distingue trois vagues. La première provient de la réduction de l'ion cobalt(II), la seconde est due probablement à certains dérivés organiques azotés. Les composés organiques sulfurés (cystéine) sont responsables de la troisième. Ces deux dernières vagues sont dites catalytiques, car leur hauteur dépasse de beaucoup celle prévue par l'équation de ILKOVIK. A même dilution, on peut provisoirement admettre que les polarogrammes sont caractéristiques de l'individu. En effet, pour une même personne, ils présentent une certaine reproductibilité.

Dans le volume II *Polarography*, I. M. KOLTHOFF ET J. J. LINGANE (1952), le lecteur trouvera clairement exposés les travaux principaux effectués sur les ondes catalytiques des protéines et des composés organiques sulfurés ainsi que sur le sérum sanguin[2].

Dans les conditions de notre travail les polarogrammes de la salive sont plus aisés à obtenir que ceux du sang puisqu'ils n'exigent pas de traitement préalable. La dénaturation de la salive n'est pas nécessaire. Après dilution on obtient donc en quelques minutes la courbe potentiel-courant d'une salive.

Appareillage et mode opératoire

Nous avons utilisé pour nos recherches le polarographe Sargent XXI, avec électrode à gouttes de mercure. Les constantes sont: temps de goutte $t = 3$ sec. Masse de mercure s'écoulant en mg/sec = 3. Hauteur du mercure $= h = 20$ cm.

Les solutions utilisées:

1) chlorure de cobalt(II) 0.008 *M*.
2) chlorure d'ammonium *M*.
3) hydroxyde d'ammonium *M*.

Bibliographie p. 582.

On introduit dans un ballon de 50 ml, 10 ml de solution 1) + 5 ml sol. 2) + 5 ml sol. 3) et on complète au trait de jauge avec de l'eau bidistillée. Avec ce mélange, on dilue la salive fraîche, non dénaturée (cette dernière s'altère assez rapidement, modification probable du système cystéine-cystine, et on observe une diminution des sauts après quelques heures déjà).

Nous avons donc entrepris, selon ce mode opératoire, l'étude systématique de la salive de trois individus différents, deux femmes et un homme. Nous désignerons ces salives par les lettres A, B et C.

Remarque

Les divers facteurs étudiés sur les polarogrammes (h, h', h'', E_1, E_2. . .) sont indiqués sur la figure 1. On remarque que la hauteur des sauts n'est pas déterminée par l'une des méthodes classiques. Il en est de même pour $E^1{}_{\frac{1}{2}}$ et $E^2{}_{\frac{1}{2}}$ qui sont obtenus en prenant le point milieu entre le départ et la fin de chaque saut.

Etude de la salive A (femme 49 ans)

Le Tableau I renferme une série de résultats tirés des polarogrammes de la salive A prise au cours de la matinée, à des jours différents. Nous avons aussi effectué le polarogramme d'un même échantillon à diverses dilutions afin de nous rendre compte de l'évolution des courbes. Il est important, en effet, pour la suite de ces recherches, de savoir si la différence obtenue entre les courbes provient de la concentration du liquide étudié dans son ensemble ou s'il y a en outre une modification dans la concentration relative des divers constituants (ou tout au moins de ceux qui se manifestent au polarographe). Le tableau suivant comprend une série de valeurs relevées sur les polarogrammes. La signification de chaque lettre est donnée dans la Fig. 1. Tous les courants sont donnés en μa. Les potentiels sont en volt, la surface du mercure dans la cuve est prise comme pôle positif.

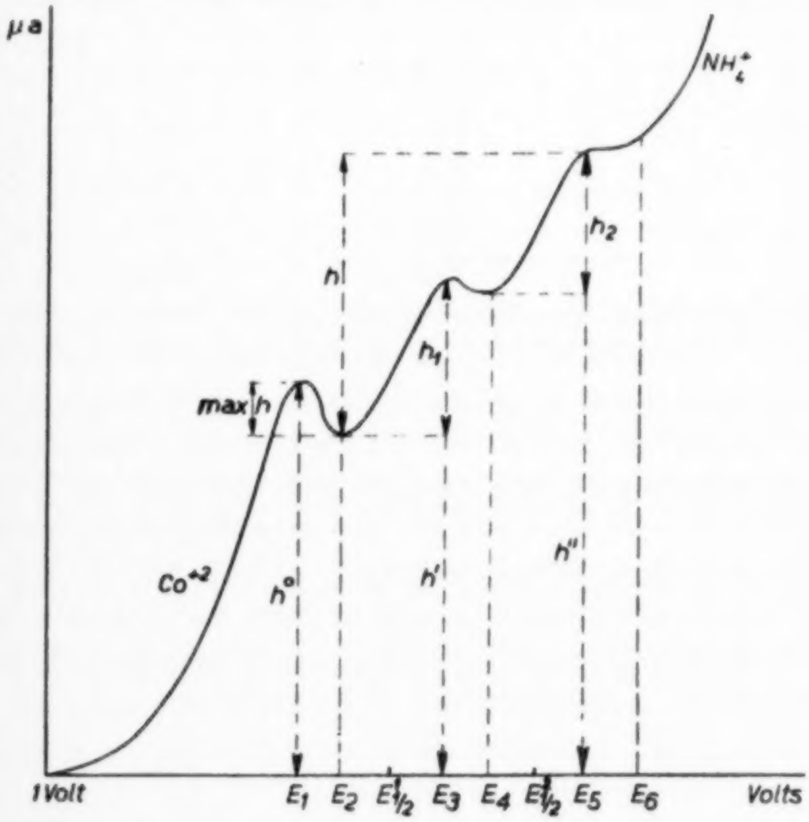

TABLEAU I

Date	h°	h′	h″	h_1	h_2	h	h_{max}	E_1	E_2	E_3	E_4	E_5	E_6	$E^{1\frac{1}{2}}$	$E^{2\frac{1}{2}}$	h_1/h_2	h′/h″	h″/h	h/h_1	S	Dil.
8/XII	9.7	12.4	20.1	2.2	7.7	10	0	1.22	1.30	1.42	1.51	1.78	1.84	1.36	1.65	0.29	0.62	2.0	4.5	0.1	20
	10.1	12.6	20.0	2.2	7.3	7.6	0	1.25	1.30	1.43	1.54	1.77	1.84	1.36	1.65	0.30	0.63	2.6	3.2	0.1	25
	11.2	11.9	16.6	1.2	5.1	6.0	0.6	1.26	1.31	1.43	1.52	1.77	1.85	1.36	1.64	0.24	0.71	2.8	5	0.1	40
	11.7	11.6	15.8	0.9	4.4	5.1	1.1	1.25	1.32	1.42	1.52	1.76	1.85	1.37	1.64	0.21	0.73	3.1	5.7	0.1	50
5/XII	10.0	14.1	21.6	3.0	7.0	10.5	0	1.26	1.33	1.45	1.52	1.78	1.80	1.36	1.68	0.4	0.65	2.1	3.5	0.1	20
	10.1	13.8	20.8	2.6	6.6	9.3	0	1.25	1.34	1.44	1.54	1.80	1.86	1.36	1.58	0.39	0.66	2.2	3.6	0.1	25
	10.6	13.6	18.4	2.3	4.3	6.4	0	1.24	1.32	1.44	1.53	1.77	1.86	1.38	1.64	0.54	0.74	2.8	2.8	0.1	30
	10.8	12.6	17.2	1.8	4.0	5.7	0	1.25	1.31	1.43	1.53	1.76	1.86	1.36	1.65	0.45	0.74	3.0	3.1	0.1	40
	10.9	12.0	16.8	1.3	4.0	5.5	0	1.26	1.32	1.42	1.55	1.79	1.86	1.37	1.70	0.32	0.72	3.1	4.2	0.1	50
	11.4	12.3	15.6	1.1	3.4	4.0	0.3	1.28	1.32	1.42	1.54	1.80	1.88	1.36	1.67	0.32	0.79	3.9	3.6	0.1	60
4/XII	8.7	11.6	17.9	2.3	6.0	7.5	0	1.23	1.30	1.42	1.52	1.78	1.84	1.36	1.63	0.38	0.65	2.4	3.3	0.1	25
	9.7	11.0	17.0	1.3	3.2	5.0	0	1.23	1.32	1.42	1.51	1.88	1.88	1.37	1.63	0.41	0.65	3.4	3.8	0.1	40
	11.6	11.4	15.0	0.8	3.5	4.2	0.7	1.24	1.30	1.40	1.51	1.75	1.87	1.35	1.63	0.23	0.76	3.6	5.3	0.1	50
	10.4	13.0	14.7	2.1	2.7	4.9	0	1.24	1.31	1.45	1.53	1.76		1.38	1.66	0.78	0.88	3.1	2.3	0.1	25
	10.2	11.9	16.0	1.6	4.2	5.8	0	1.25	1.31	1.43	1.51	1.80	1.87	1.36	1.66	0.38	0.74	2.8	3.6	0.1	40
	11.5	11.5	14.7	1.0	3.3	4.1	0.9	1.26	1.31	1.44	1.53	1.80	1.87	1.37	1.66	0.30	0.78	3.6	4.1	0.1	50
20/XI	10.4	15.2	28.0	3.6	13.0	16.8	0	1.24	1.32	1.44	1.51	1.79	1.87	1.38	1.64	0.28	0.54	1.7	4.7	0.2	15
	11.1	14.7	25.5	2.6	10.7	13.1	0	1.23	1.32	1.42	1.52	1.77	1.86	1.37	1.64	0.24	0.58	1.9	5.0	0.1	20
	12.7	15.4	24.7	1.9	9.2	11.4	0	1.26	1.32	1.44	1.52	1.79	1.86	1.38	1.65	0.21	0.62	2.2	6.0	0.1	25
	13.5	15.0	23.4	1.7	8.2	9.8	0	1.26	1.31	1.45	1.53	1.80	1.88	1.38	1.65	0.21	0.64	2.4	5.7	0.1	30
	13.4	13.9	19.8	1.1	6.1	7.0	0.7	1.25	1.31	1.44	1.52	1.79	1.85	1.37	1.64	0.18	0.70	2.8	6.2	0.1	40
	19.0	12.4	18.6	0.24	5.0	5.2	5.4	1.27	1.34	1.41	1.51	1.78	1.86	1.38	1.64	0.04	0.67	3.6		0.08	60
9/XII	9.6	13.2	20.7	2.3	6.8	10.2	0	1.28	1.33	1.44	1.55	1.80	1.89	1.40	1.67	0.34	0.64	2.1	4.5	0.1	20
	9.8	12.7	20.1	2.3	6.8	10.1	0	1.26	1.30	1.42	1.53	1.80	1.88	1.38	1.67	0.34	0.61	2.0	4.5	0.1	25
	10.1	11.4	16.1	1.2	4.8	6.1	0	1.26	1.31	1.42	1.54	1.80	1.87	1.34	1.67	0.25	0.71	2.7	5.1	0.1	40
	10.4	10.0	15.0	0.9	4.2	4.7	0.3	1.27	1.33	1.44	1.54	1.79	1.86	1.37	1.67	0.21	0.67	3.2	5.2	0.1	50
	10.0	10.9	14.7	0.8	3.8	4.6	0.6	1.27	1.33	1.44	1.53	1.79	1.86	1.38	1.66	0.21	0.74	3.2	5.8	0.08	60

L'examen du tableau précédent conduit aux remarques suivantes:

1) les vagues étant d'origine catalytiques, on ne peut espérer une rigoureuse reproductibilité pour une même salive prélevée à des jours différents, étudiée dans les mêmes conditions.

2) A très faible dilution (10 dans le cas présent), les polarogrammes sont extrêmement touffus, ils ne peuvent être pris en considération.

3) Les potentiels de début et de fin de saut, de même que les valeurs des $E_{1/2}$ ne subissent que des faibles variations lorsqu'on passe d'un échantillon à l'autre, même si les dilutions sont très différentes. Sur 38 courbes effectuées sur la salive A, les différents potentiels sont compris entre les valeurs extrêmes suivantes:

E_1 de 1.22 à 1.28 volt
E_2 de 1.30 à 1.33 volt
E_3 de 1.42 à 1.45 volt
E_4 de 1.51 à 1.54 volt
E_5 de 1.76 à 1.80 volt
E_6 de 1.80 à 1.88 volt
$E^1{}_{1/2}$ de 1.34 à 1.40 volt
$E^2{}_{1/2}$ de 1.64 à 1.67 volt

Si l'on tient compte du fait que la mesure exacte des potentiels n'est pas toujours facile, que, d'autre part, la présence des maximum du cobalt perturbe quelque peu la courbe, que ces potentiels sont déterminés pour des dilutions variant de 15 à 60 et qu'enfin ils sont pris par rapport à la surface de mercure de la cuve polarographique, on peut considérer que leur valeur présente une bonne reproductibilité.

La différence entre les potentiels consécutifs oscillent aussi entre d'étroites limites:

$E_2 - E_1$ de 0.05 à 0.08 volt
$E_3 - E_2$ de 0.10 à 0.14 volt
$E_4 - E_3$ de 0.07 à 0.13 volt
$E_5 - E_4$ de 0.23 à 0.29 volt
$E_6 - E_5$ de 0.07 à 0.09 volt
$E^2{}_{1/2} - E^1{}_{1/2}$ de 0.26 à 0.32 volt

4) Le saut du cobalt présente, aux dilutions les plus fortes, un maximum qui peut être très marqué et dont la hauteur varie pour une même dilution. La diminution de la concentration de protéine n'est probablement pas le seul facteur responsable de ce phénomène. Les autres vagues n'ont pas de vrais maximum, bien que souvent, on observe une diminution passagère du courant après les sauts catalytiques.

5) Si l'on fait le graphique des sauts h_1 et h_2 en fonction de la concentration de la salive, on observe que h_2 diminue beaucoup plus rapidement que h_1, mais cet abaissement du courant n'est pas rigoureusement proportionnel.

6) Afin de rechercher les constantes éventuelles de la salive, nous avons calculé un certain nombre de rapports: h_1/h_2, h'/h'', h''/h et h/h'. Pour tous les polarogrammes de la salive A, ces rapports sont compris entre les limites suivantes:

h_1/h_2 de 0.18 à 0.54 h'/h'' de 0.63 à 0.93
h''/h de 1.9 à 5 h'/h de 2.8 à 6

Il sera intéressant de comparer ces valeurs avec celles obtenues pour d'autres individus.

Etude de la salive B (homme 49 ans), voir Tableau II.

1) et 2) mêmes remarques que pour la salive A.

3) Même remarques que pour la salive A, les valeurs des potentiels sont comprises pour

E_1 entre 1.21 et 1.27 volt E_2 entre 1.28 et 1.32 volt
E_3 entre 1.41 et 1.47 volt E_4 entre 1.52 et 1.56 volt
E_5 au voisinage de 1.65 (souvent difficile à mesurer)
E_6 entre 1.74 et 1.80 volt $E^1{}_{1/2}$ entre 1.36 et 1.40 volt
$E^2{}_{1/2}$ entre 1.58 et 1.61 volt.

Le E_6 qui correspond au potentiel de départ de l'ion NH_4^+ est le moins constant, il n'est pas toujours aisé à mesurer. La plupart de ces potentiels sont très voisins de ceux de la salive précédente. Pourtant on remarque une nette différence pour E_5 et pour $E^2{}_{1/2}$ qui permet de distinguer sans hésitation possible ces deux salives, quelle que soit leur dilution. Quant aux différences entre les potentiels, elles ont pour limites:

$E_2 - E_1$ 0.04 à 0.09 $E_3 - E_2$ 0.08 à 0.16 $E_4 - E_3$ 0.08 à 0.13
$E_5 - E_4$ 0.14 à 0.17 $E_6 - E_5$ 0.06 à 0.12 $E^2{}_{1/2} - E^1{}_{1/2}$ 0.25 à 0.28 volt,

Là encore, on observe une importante différence avec la salive A pour $E_5 - E_4$ pour lesquelles les limites ne se recouvrent pas.

4) Une représentation graphique de h_1 et h_2 en fonction de la dilution conduit aux mêmes remarques que celles faites pour la salive A, mais les courbes, particulièrement celle de h_2 se trouvent dans des régions très différentes. De plus les valeurs de h_2 et h_1 sont inversées, on a $h_2{}^A > h_1{}^A$ et $h_2{}^B < h_1{}^B$ ce qui permet de les différencier sans ambiguïté.

5) La valeur de rapports

h_1/h_2 est comprise pour toutes les salives B entre	1 et 2.8
h'/h''	0.84 et 0.99
h''/h	2.5 et 8.9
h/h'	1.2 et 1.6

Comme on le voit, les valeurs des rapports h_1/h_2 et h'/h'' ne se recouvrent pas dans le cas des deux salives, quant à h''/h il est en général plus élevé pour B que pour A.

Ainsi donc ces deux salives ne peuvent être confondues au polarographe, quelle que soit la dilution ou le jour d'échantillonnage.

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TABLEAU II

Date	h°	h′	h″	h_1	h_2	h	h_{max}	E_1	E_2	E_3	E_4	E_5	E_6	$E^{1}_{1/2}$	$E^{2}_{1/2}$	h_1/h_2	h′/h″	h″/h	h/h_1	Dil.
15/XII	10.0	14.4	14.7	3.4	1.8	4.5	0	1.24	1.28	1.44	1.52	1.65	1.84	1.36	1.59	1.90	0.99	3.2	1.4	20
	13.1	12.2	12.8	1.35	1.04	2.0	2.3	1.25	1.32	1.43	1.53	1.65	1.82	1.37	1.60	1.30	0.96	6.3	1.5	40
	14.1	11.9	12.6	1.0	0.93	1.7	3.5	1.25	1.32	1.41	1.50	1.64	1.82	1.37	1.58	1.18	0.95	7.4	1.7	50
	8.7	14.7	17.5	5.0	2.8	7.7	0	1.22	1.29	1.44	1.52	1.65	1.84	1.38	1.60	1.8	0.85	2.3	1.5	10
16/XII	8.9	14.5	16.2	4.7	1.7	6.4	0	1.21	1.30	1.45	1.52	1.65	1.74	1.39	1.60	2.8	0.9	2.5	1.4	10
	10.4	12.2	14.6	3.4	1.3	4.0	0	1.26	1.31	1.45	1.54	1.65	1.75	1.39	1.60	2.6	0.84	3.7	1.2	20
	12.8	11.2	11.5	1.0	0.72	1.3	2.7	1.30	1.36	1.46	1.56	1.66	1.84	1.40	1.61	1.4	0.98	8.9	1.3	40
	15.5			0.8	0.6	1.0	5.0	1.27	1.33	1.46	1.55	1.66	1.78		1.60	1.65			1.3	50
17/XII	10.6	13.4	14.0	3.0	1.4	3.8	0	1.25	1.31	1.44	1.52	1.66	1.81	1.37	1.60	2.1	0.96	3.7	1.3	20
	15.1	12.0	12.7	0.88	0.88	1.44	4	1.26	1.34	1.42	1.52	1.64	1.80	1.38	1.59	1.0	0.95	8.2	1.6	40
	18.0	11.5	11.9	0.24	0.64	0.48	6.8	1.27	1.36	1.44	1.53	1.65	1.80	1.39	1.60	0.4	0.98	2.3		50
	8.7	14.0	15.6	4.4	1.9	6.0	0	1.23	1.32	1.47	1.54	1.66		1.39	1.60	2.3	0.90	2.6	1.4	10

TABLEAU III

Date	h°	h′	h″	h_1	h_2	h	h_{max}	E_1	E_2	E_3	E_4	E_5	E_6	$E^{1^1/_2}$	$E^{2^1/_2}$	h_1/h_2	h′/h″	h″/h	h/h_1	S	Dil.
25/XI	13.4	16.0	20.5	1.8	4.5	6.2	0	1.25	1.31	1.43	1.54	1.78		1.38	1.64	0.4	0.78	3.3	3.4	0.1	50
	16.1	15.7	17.2	0.96	2.4	2.9	1.36	1.26	1.32	1.42	1.53	1.78	1.84	1.38	1.65	0.4	0.92	5.8	3.0	0.08	120
	15.1	15.9	18.2	1.36	2.7	3.8	0.48	1.27	1.32	1.43	1.52	1.78	1.84	1.37	1.65	0.5	0.87	4.7	2.8	0.08	100
	14.2	17.4	21.4	2.5	4.2	6.5	0	1.27	1.33	1.46	1.54	1.78	1.86	1.40	1.66	0.6	0.82	3.3	2.6	0.1	60
	15.1	16.7	19.5	1.6	3.1	4.4	0	1.27	1.32	1.44	1.53	1.78	1.84	1.37	1.65	0.52	0.86	4.5	2.8	0.1	80
	10.5	11.7	14.0	1.3	2.5	3.5	0	1.26	1.33	1.43	1.54	1.78	1.88	1.38	1.66	0.52	0.85	4.0	2.7	0.08	50
	11.7	11.2	12.7	0.9	1.8	2.4	1.3	1.28	1.35	1.44	1.54	1.78	1.88	1.46	1.66	0.50	0.88	5.3	2.7	0.08	75
	13.7	10.7	11.8	0.4	0.96	1.3	3.5	1.28	1.36	1.44	1.52	1.78	1.88	1.40	1.65	0.42	0.91	9.2	3.2	0.08	100
	10.7	11.0	12.7	0.9	2.1	2.8	0.6	1.27	1.34	1.44	1.53	1.78	1.88	1.40	1.66	0.43	0.86	4.6	3.1	0.08	60
11/XII	10.6	12.3	14.7	1.7	2.6	4.1	0	1.26	1.30	1.43	1.51	1.78	1.87	1.36	1.66	0.60	0.84	3.6	2.4	0.08	40
	11.1	11.9	14.4	1.2	2.5	3.7	0.5	1.27	1.31	1.44	1.52	1.78	1.90	1.38	1.65	0.48	0.83	3.9	3.1	0.08	50
	11.5	11.1	13.2	0.8	2.2	2.8	1.3	1.25	1.33	1.42	1.51	1.78	1.88	1.38	1.65	0.37	0.84	4.7	3.5	0.08	60
	14.1	11.2	12.6	0.5	1.9	2.1	3.4	1.26	1.35	1.43	1.52	1.78	1.89	1.39	1.64	0.26	0.89	6.0	4.3	0.08	80
12/XII	10.9			1.7	3.4	4.6	0	1.27	1.31	1.44	1.52	1.78	1.90	1.40	1.65	0.50			2.7	0.08	40
	11.7	13.2	16.0	1.4	3.2	4.4	0	1.27	1.33	1.44	1.52	1.78	1.86	1.38	1.65	0.43	0.83	3.7	3.1	0.08	50
	11.7	12.0	14.6	1.0	2.6	3.4	0.6	1.25	1.31	1.42	1.50	1.78	1.86	1.36	1.64	0.39	0.82	4.2	3.4	0.08	60
	13.5	12.0	13.9	0.64	1.92	2.5	2.2	1.27	1.31	1.43	1.51	1.78	1.88	1.38	1.65	0.33	0.87	5.5	3.9	0.08	80

Etude de la salive C (femme 27 ans), voir Tableau III.

Les polarogrammes de cette salive se rapprochent sensiblement de ceux de la salive A. En effet, E_1 varie de 1.25 à 1.28, E_2 de 1.31 à 1.35, E_3 de 1.41 à 1.46, E_4 de 1.51 à 1.54, E_5 ne peut être mesuré exactement, E_6 de 1.84 à 1.90 volt, $E^1{}_{1/2}$ de 1.36 à 1.44 et $E^2{}_{1/2}$ de 1.64 à 1.66 volt.

En ce qui concerne les sauts, on observe qu'il est impossible d'avoir une courbe bien dessinée pour des dilutions plus faibles que 40 alors que dans les deux cas précédents, on obtient des polarogrammes encore utilisables pour des dilutions de 15. Ce phénomène n'est pas dû à une trop grande concentration des constituants puisqu'à ce point de vue il n'y a pas une grande différence entre les salives A et C. Cette dernière par contre donne encore de bonnes courbes à des dilutions de 100, alors qu'on ne dépasse pas 60 dans les autres essais. En outre le rapport h_1/h_2 est en général plus grand pour C que pour A. Pourtant dans quelques cas les valeurs se superposent. Il est évident que si au lieu de prendre les limites extrêmes des diverses valeurs étudiées, on raisonnait sur la moyenne, on obtiendrait des différences beaucoup plus marquées mais ceci implique l'obligation d'effectuer un grand nombre de polarogrammes, ce qui complique quelque peu la détermination.

Remarques

En résumé nous pouvons faire les observations suivantes:

1) Les trois salives étudiées présentent suffisamment de différences pour pouvoir être identifiées au polarographe.

2) Pour les trois salives le rapport h'/h'' est toujours compris entre 0.63 et 0.99, quelle que soit la dilution.

3) Le nombre de cas étudiés est trop restreint pour nous permettre d'énoncer des principes généraux. Nous allons poursuivre cette étude sur un grand nombre de cas, tout d'abord de personnes saines de divers âges et des deux sexes, puis sur des personnes atteintes d'affections susceptibles d'agir sur le système glandulaire. Il serait intéressant d'entreprendre une série de déterminations sur la salive de personnes atteintes de cancer et de comparer les résultats avec ceux obtenus avec le sérum sanguin[2].

4) Il y a d'autres moyens de différencier les salives et qui peuvent donner des renseignements intéressants sur la constitution de celles-ci. En effet, nous avons effectué quelques essais de dénaturation et constaté que les sauts en sont modifiés. C'est ainsi que la salive A qui donne pour h_1 2.3 μa et pour h_2 4.3 μa voit ses sauts augmenter sensiblement après une dénaturation de une heure à 80° h_1 passe à 2.8 μa et h_2 à 4.8 μa avec une augmentation du rapport h_1/h_2. Des observations analogues ont été faites sur le sérum sanguin[2]. Des déterminations systématiques seront entreprises dans un prochain travail.

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TABLEAU IV

Glandes	h°	h′	h″	h_1	h_2	h	h_{max}	E_1	E_2	E_3	E_4	E_5	E_6	$E^{1\frac{1}{2}}$	$E^{2\frac{1}{2}}$	h_1/h_2	h′/h″	h″/h	h/h_1	S	Dil.
Parotide Gauche	9.2	10.5	13.8	1.75	3.1	4.6	0	1.25	1.25	1.40	1.52	1.77	1.86	1.34	1.67	0.57	0.77	3.1	2.6	0.08	25
,,	9.2	10.7	14.1	1.52	3.3	5.0	0	1.27	1.27	1.42	1.58	1.77	1.89	1.36	1.67	0.46	0.77	2.8	3.2	0.08	52
Droite	9.1	11.3	14.9	2.1	3.4	5.7	0	1.25	1.25	1.42	1.51	1.78	1.86	1.34	1.65	0.62	0.76	2.6	2.7	0.08	25
Parotides G et D	10.0	12.1	16.4	2.4	3.7	6.2	0	1.27	1.27	1.45	1.52	1.80	1.86	1.36	1.67	0.65	0.75	2.6	2.7	0.08	25
Gauche	9.2	10.3	14.0	0.96	3.5	4.6	0	1.28	1.28	1.42	1.54	1.79	1.89	1.35	1.66	0.27	0.74	3.1	4.7	0.08	30
,,	9.3	9.9	12.7	0.64	2.7	3.5	0	1.30	1.30	1.42	1.56	1.81	1.92	1.36	1.68	0.24	0.78	3.6	5.5	0.08	40
,,	9.3	9.7	11.6	0.24	1.92	2.0	0	1.31	1.31	1.45	1.57	1.80	1.91	1.39	1.69	0.13	0.84	5.8	8.4	0.08	50
,,	10.0	9.3	10.9	0.24	1.52	1.84	0.32	1.30	1.32	1.44	1.56	1.79	1.86	1.40	1.67	0.16	0.83	5.9	7.6	0.08	60
Sublinguale	13.2	12.1	14.2	1.4	2.7	3.4	2.4	1.26	1.33	1.44	1.52	1.76	1.80	1.40	1.64	0.51	0.85	4.2	2.6	0.08	50
,,	11.4	11.1	14.3	1.3	2.9	3.9	1.7	1.25	1.33	1.42	1.52	1.73	1.80	1.38	1.63	0.45	0.78	3.7	3.0	0.08	50
,,	11.8	10.7	12.6	1.1	2.0	2.7	2.2	1.25	1.34	1.42	1.52	1.76	1.81	1.39	1.64	0.56	0.85	4.8	2.4	0.08	
,,	15.7	10.8	12.6	0.9	2.0	2.6	5.6	1.27	1.35	1.43	1.52	1.75	1.80	1.40	1.63	0.44	0.86	4.9	2.9	0.08	50
Deux Jumelles Josepha	10.1	14.3	17.3	3.8	3.0	6.5	0	1.24	1.28	1.44	1.51	1.66	1.76	1.36	1.60	1.27	0.83	2.7	1.7	0.1	25
Ilda	10.0	14.0	17.0	3.8	2.8	6.5	0	1.26	1.29	1.45	1.52	1.66	1.76	1.37	1.61	1.37	0.83	2.6	1.7	0.1	25

Etude polarographique de chaque glande salivaire séparée

Contrairement à ce que nous avions supposé, l'étude séparée de chaque glande n'a pas apporté les résultats espérés. En effet, les polarogrammes ne présentent pas une plus grande reproductibilité pour chaque glande que ceux provenant d'une salive moyenne. A titre documentaire, nous donnons quelques résultats obtenus sur la salive d'une personne A, Tableau IV.

Nous n'avons pas donné les résultats obtenus pour les sauts de la salive sous-maxillaire car les polarogrammes ne se prêtent pas à des mesures suffisamment précises. Par contre, pour les 2 autres glandes, on constate que la constitution de la salive est différente. Pour la parotide, E_1 et E_2 sont confondues. D'autre part la sublinguale donne des maximum très marqués à la dilution 50 alors que ceux-ci n'apparaissent que faiblement pour la dilution 60 dans le cas de la parotide. On observe une différence sensible aussi dans les $E^{1}{}_{1/2}$ et $E^{2}{}_{1/2}$, de même que pour E_6. Il nous semble préférable d'effectuer l'étude systématique de la salive sur un mélange de salive provenant de différentes glandes.

Grâce au Dr. GEORGES NICOLAS, il nous a été possible d'effectuer le polarogramme de la salive totale de 2 groupes de jumelles. Dans le premier cas, ces salives, diluées 25 fois, donnent des polarogrammes absolument identiques. Les 2 courbes sont pratiquement superposables et les rapports sont égaux (voir Tableau IV). Pour 2 autres jumelles par contre, les résultats sont moins remarquables, bien qu'il y ait une grande analogie entre les courbes. Malheureusement, ces dernières sont mal dessinées et la fin du 3ème saut, ainsi que le départ du saut de l'ion ammonium, ne sont pas perceptibles. De plus, on observe, pour certaines dilutions, un maximum qui perturbe la courbe.

Nous poursuivrons également des recherches dans cette direction.

RÉSUMÉ

La salive diluée (20 à 100 fois) donne, en présence de chlorure de cobalt, de chlorure d'ammonium et d'ammoniaque, 3 sauts dont les 2 derniers sont d'espèce catalytique. L'étude systématique de la salive de 3 personnes a été entreprise dans ces conditions. Il est montré que, quelle que soit la dilution, il est possible de déterminer l'origine de chaque salive. Il y a donc une certaine reproductibilité des polarogrammes pour un individu déterminé. L'étude sera poursuivie sur un grand nombre d'individus, pour mettre en évidence si possible quelques caractéristiques spécifiques de la salive de personnes saines, afin de voir comment celle-ci se modifie au cours de diverses maladies.

SUMMARY

Saliva diluted 20-100 times gives, in the presence of cobalt chloride, ammonium chloride and ammonia, three jumps of which the last two are of catalytic nature. The systematic study of saliva obtained from three persons has been undertaken under these conditions. It is shown that whatever be the dilution it is possible to determine the origin of each saliva. There is, therefore, a certain reproducibility of polarograms for a definite individual. The study will be followed up on a large

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number of individuals, in order to demonstrate, if possible, some specific characteristics of the saliva of healthy people, and so to observe how this changes in the course of different illnesses.

ZUSAMMENFASSUNG

20 bis 100 mal verdünnter Speichel zeigt in Gegenwart von Cobaltchlorid, Ammoniumchlorid und Ammoniak 3 Sprünge, von denen die 2 letzten katalytischer Art sind. Die systematische Untersuchung des Speichels von 3 Personen wurde bei diesen Bedingungen unternommen. Es wurde gezeigt, dass es möglich ist, ganz gleich bei welcher Verdünnung, die Herkunft des Speichels zu bestimmen. Es besteht folglich eine gewisse Reproduzierbarkeit des Polarogramms für ein bestimmtes Individuum. Die Untersuchung wird auf einen grösseren Personenkreis ausgedehnt, um, wenn möglich, einige spezifische Eigenschaften des Speichels gesunder Personen aufzuzeigen und zu sehen, wie diese sich im Verlauf der verschiedenen Krankheiten verändern.

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Reçu le 13 janvier 1953

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Ordinary Meeting of the Society

An Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, April 1st, 1953, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the President, Dr. D. W. KENT-JONES, F.R.I.C., and 147 members and visitors were present.

The subject of the meeting was *The Determination of Small Amounts of Lead in Foods and Biological Materials* and the following papers were presented and discussed:

A Reversion Method for the Absorptiometric Determination of Traces of Lead with Dithizone, by H. M. IRVING, M.A., D. Phil., F.R.I.C., L.R.A.M., and E. J. BUTLER, B.A., B.Sc., D. Phil., A.R.I.C.

A method was described for the determination of lead in small samples of biological materials. The procedure involves wet ashing of the sample, extraction of all the lead (and any bismuth present) with dithizone, a preliminary separation from the bulk of the bismuth, and a final absorptiometric determination of lead by the "reversion" technique.

Quantities of lead in the range of 0 to 2μg can be determined satisfactorily in the presence of up to 20μg of bismuth and at least 100μg of copper and zinc.

Preparation of Samples of Foodstuffs and Biological Materials for the Determination of Lead, by R. F. MILTON, B.Sc., Ph. D., F.R.I.C. (Presented by K. J. JARRETT, B.Sc., A.R.I.C.).

Some of the possible causes of error in the micro-estimation of lead were outlined. In the ignition procedure losses are due to volatilisation of lead and fusion of lead into the body of the crucible.

In the wet oxidation procedure the introduction of quantities of lead (via reagents) of the same order as that to be estimated may occur, and this gives rise to large difference errors. An alternative method suggested is based on the preparation of an acid extraction after the foodstuff has been partially digested by acid hydrolysis under pressure. The filtered extract is then treated with dithizone in chloroform to concentrate and remove lead from extraneous matter prior to estimation.

Sample Preparation for Determination of Lead in Foodstuffs, by D. A. ELVIDGE, B.Sc., AND D. C. GARRATT, B.Sc., Ph.D., F.R.I.C.

Owing to the high blanks obtained on normal wet combustion of foodstuffs, a new approach to the problem of sample preparation was suggested. The substance is combusted in an atmosphere of oxygen inside a stainless steel bomb. The lead is subsequently obtained in solution and can be determined in a number of ways.

Annual General Meeting of the Polarographic Discussion Panel

The Annual General Meeting of the Polarographic Discussion Panel of the Physical Methods Group of the Society was held at 6.30 p.m. on Wednesday, December 3rd, 1952, at the Sir John Cass College, Jewry Street, London, E.C. 3.

The following were elected Officers of the Panel for the ensuing year: —

Chairman — Dr. A. J. LINDSEY
Hon. Secretary — Mr. G. W. C. MILNER, Building 148, A.E.R.E., Harwell, Nr. Didcot, Berks.

The business meeting was followed by an Ordinary Meeting of the Panel, at which the following papers were presented and discussed:

Modification of the Cambridge Polarograph for Derivative Polarography, by P.R.D. POMEROY, B.Sc., AND R. A. WHITE.

A simple adaptor converts a Cambridge photographic recording polarograph to the derivative type described by LEVEQUE AND ROTH in which the normal wave is replaced by a peak at the same potential.

Derivative polarography has been found to have the following advantages: (1) The accuracy and ease of measurement for a given concentration of an ion is substantially independent of the concentration of ions polarising at lower potentials; (2) it is possible to separate and measure peaks caused by ions whose half wave potentials are about the same; (3) the accuracy of measurement for ions giving poorly defined waves is greatly increased.

A modified dropping mercury electrode virtually eliminates the "drop oscillations".

The Polarographic Determination of Cadmium in Aluminium and Some Other Alloys, by W. STROSS, M.D., F.R.I.C.

The author's procedure for polarographic determination of cadmium in aluminium alloys* was discussed.

Essentially the same procedure appears to be applicable to the determination of cadmium as impurity in copper; the same process can also serve to determine with practically no extra work a number of other impurities. As these determinations of impurities are carried out in the electrolyte, all this can, by selecting a suitable medium for the electrolysis, be combined with the determination of the copper content. Very low contents (0.001 per cent. and below) can be determined.

The determination of cadmium in magnesium alloys was also discussed.

Ordinary Meeting of the Society

An Ordinary Meeting of the Society was held at 7 p.m. on Wednesday, May 20th, 1953, in the Meeting Room of the Chemical Society, Burlington House, London W.1. The President Dr. D. W. KENT-JONES, F.R.I.C., was in the Chair, and the following papers were presented and discussed:

The Determination of Ergosterol in Yeast, by W. H. C. SHAW, Ph.C., F.R.I.C., and J. P. JEFFERIES, B.Sc., A.R.I.C.

Part I. The Ultra-violet Absorption of Purified Ergosterol

Most published records agree on the wavelengths of the three main peaks in the ultra-violet absorption curve of ergosterol, but there are discrepancies in the extinction values reported for the various maxima, apparently because of the difficulty of preparing pure ergosterol by direct recrystallisation of the commercial material and to a lesser extent because of small variations in the moisture content of the hydrated sterol. Simple recrystallisation does not always yield a pure product; the best means of purification is by recrystallising a suitable ester, with subsequent regeneration of the sterol.

The preparation and purification of ergosterol benzoate was described and the physical properties and ultra-violet absorption (in various solvents) of a purified specimen of ergosterol were recorded.

Part II. Determination by Saponification and Ultra-violet Absorption Spectroscopy

Part of the ergosterol found in yeast occurs in a combined form, and treatment to liberate the free sterol is a necessary preliminary to its determination. Most published methods make use of alcoholic or aqueous alkali hydroxides for this purpose, and the variety of strengths prescribed suggested that further investigation was necessary.

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* *Metallurgia,* 43 (1951) 145. *Proceedings International Congress of Polarography,* Prague, 1951, page 397.

The conditions for the destruction of the yeast cells and maximum recovery of ergosterol have been studied. It was found that boiling under reflux with alcoholic sodium or potassium hydroxides did not break down the yeast sufficiently. Aqueous sodium hydroxide at strengths from 10 to 50 per cent. w/w gave low and erratic results, additional ergosterol being recovered by subsequent alcoholic saponification of the residue.

Concentrations of potassium hydroxide above 20 per cent. w/w in aqueous solution proved satisfactory, the strength required depending on the length of boiling under reflux. For the method descrbed 40 per cent. w/w aqueous potassium hydroxide has been selected, as it makes possible considerable latitude in time and concentration.

The ergosterol in the extracted unsaponifiable matter is separated by digitonin precipitation from non-sterol substances that show irrelevant absorption in the same region as ergosterol. This precipitation has been shown to be quantitative, the separated sterol digitonides yielding solutions spectroscopically indistinguishable at wavelengths above 260 mμ from those of purified ergosterol.

Part III. Corrections for Irrelevant Absorption in Solutions of Ergosterol

The unsaponifiable matter of yeast normally contains substances that possess ultra-violet absorption in the same region as ergosterol, so that the extinction at the ergosterol maximum (282 mμ in absolute alcohol) cannot be used directly as a measure of the concentration of ergosterol present. Although the digitonin purification described in Part II may be used for separating ergosterol in a spectroscopically pure condition, considerable time can be saved by applying a correction procedure to the gross absorption.

Two such procedures have been studied: (i) a correction of the Morton and Stubbs type, based on the 282-mμ maximum and two subsidiary wavelengths at which the purified compound possesses 6/7 maximum absorption, and (ii) a new four-point correction based on the three ergosterol maxima (271.5, 282, and 293.5 mμ) with a fourth reading at 310 mμ, where ergosterol shows very little absorption.

Procedure (i) suffers from the disadvantage that the maxima in the absorption curve of ergosterol are sharp and observations at the subsidiary wavelengths must be taken on steep portions of the curve. In consequence small errors in measuring wavelengths have a large effect on the correction factor and any instrument used for this procedure must be calibrated with pure ergosterol. Procedure (ii) is free from this disadvantage but requires a greater range of wavelengths and linearity of absorption must be assumed over it.

Results by both corrective procedures were compared with those by the full digitonin method previously described. The degree of agreement is generally good, but depends on the shape and amount of irrelevant absorption, which has been determined on a number of different strains of yeasts.

Part IV. A Short Method Based on Ultra-violet Absorption

An accurate method for determining ergosterol in yeast has been described in Part II; it involves saponification, extraction of unsaponifiable matter, digitonin precipitation and subsequent spectroscopic determination and has proved too lengthy for the examination of large numbers of samples.

For this purpose, a short semi-micro method was described: it involves saponifying a portion of the yeast sample containing about 1 mg of ergosterol with a small volume of 40 per cent. w/w aqueous potassium hydroxide in a specially designed flask and extracting the unsaponifiable matter with a single accurately measured volume of cyclohexane. The filtered extract is suitable for spectroscopic examination. The fourpoint correction procedure described in Part III is applied to allow for irrelevant absorption; the ergosterol content of the sample is calculated from the corrected extinction at 282 mμ (max.).

The method requires much less manipulation time than the full digitonin procedure but, because a geometrical correction and a single extraction only are used, gives results slightly lower and a standard deviation of a single determination a little greater than are got with the full method.

The Estimation of Micro Quantities of Calcium, by G. E. HARRISON, Ph.D., F.Inst.P., and W. H. A. RAYMOND.

A micro method for the estimation of calcium was described; it is based on the colorimetric estimation of a molybdenum thiocyanate. An accuracy of better than 10 per cent. is attained for solutions containing as little as 4 μg of calcium.

The method is especially useful for the estimation of serum calcium in young children or small laboratory animals.

A comparison of the results with those found by other methods was given.

The Ultra-violet Spectrophotometric Estimation of the Quality of Mineral Oils Extracted from Bread, by M. A. COOKSON B.Sc., A.R.I.C., J. B. M. COPPOCK, B.Sc.,Ph.D., F.R.I.C., and R. SCHNURMANN, M.Sc., Dr.Rer.Nat.

A method has been developed by which the degree of refining of a mineral oil that has been absorbed by a dough during bread making may be determined in the resultant bread. The method consists basically of sulphating, under controlled conditions, the unsaponifiable fraction of the total oils extracted from bread, so that the natural saponifiable matter is destroyed without completely removing the unsaturated hydrocarbon constituents inherent in mineral oils of different degrees of refining. The recovered mineral oil is then examined by ultra-violet absorption spectrophotometry to determine its quality. A spectrophotometric criterion was suggested for the quality of mineral oils that could be regarded as satisfactory for the lubrication of plant used in bread production.

Joint Meeting of the Physical Methods Group

The Forty-first Ordinary Meeting of the Physical Methods Group of the Society was held at 6.00 p.m. on Friday, May 8th, 1953, in the Oriental Cafe, Ipswich. This was a joint meeting with the East Anglian Section of the Royal Institute of Chemistry. Dr. J. HASLAM was in the Chair and about 38 members and visitors were present.

The following papers on *Emission Spectroscopy* were presented and discussed.

Semiquantitative Techniques in Spectrochemical Analysis, by R. L. MITCHELL, B.Sc., Ph.D., F.R.I.C.

There is often a need for something between a purely qualitative examination of a sample and an exact, time-consuming, quantitative determination of one or more consituents. Several spectrochemical procedures which can provide the necessary information have been described. In this respect spectroscopic methods are generally somewhat more flexible than other analytical procedures. The semi-quantitative approach is particularly valuable for the survey of a number of constituents in a large number of samples.

The approach to the problem has varied with different workers, and several of the methods suggested were reviewed. That in use at The Macaulay Institute for Soil Research for estimations of this type, particularly in soils, rocks and minerals involves cathode layer excitation, followed by visual comparison of the spectrograms, with those of standard samples of like matrix composition in a spectral line comparator.

Some Techniques of Presentation of Sample to the Spectrograph, by A. H. C. P. GILLIESON, B.Sc., Ph.D.

Four methods of sample presentation were described — three arc and one spark.

They are all essentially methods for detection and estimation of trace elements; two are quantitative, the others semiquantitative.

1. Copper-Arc using Flux plus sample.
2. Carrier-Distillation D.C. Graphite Arc.
3. Hollow Cathode Discharge Tube.
4. Copper Spark plus Sample Solution.

The first is a quantitative method of wide application suitable for a wide variety of element oxides or other compounds, *e.g.* plant ashes, ignited soils, and ores.

The second is suitable for the determination of impurities in refractories, *e.g.* alumina, beryllia, etc.

The third, for which solid samples or solutions may be used, is particularly useful for the determination of the halides, but will also determine the alkali metals and sulphur. It can be applied direct to organic materials.

The last — a solution method — is of wide application where the amount of material available is very small in quantity.

Applications of the Porous Cup Technique, by L. G. YOUNG.

A modification of the porous cup technique of FELDMAN has been applied to the determination of a major constituent — zinc in brass. Details include the preparation of electrodes, analytical procedure and a new electrode stand designed for this work. Tables showing the reproducibility and accuracy of single determinations were presented. Mention is made of other metallurgical samples analysed and of various difficulties already overcome in the application of the method to the complete analysis of soluble miscellaneous residues, ashes and corrosion products.

The meeting was preceded by a visit to the Research Laboratories of B.X. Plastics, Manningtree.

Ordinary Meeting of the Society

An Ordinary Meeting of the Society (organised jointly by the Microchemistry Group and the Scottish Section) was held at 7.15 p.m. on Wednesday, May 6th, 1953, in the Chemistry Departement, University of Glasgow. Chair The was taken by the President, Dr. D. W. KENT-JONES, F.R.I.C., and the following papers were presented and discussed:

Geochemistry and Microchemistry, by DAVID T. GIBSON, D.Sc.

Many of the most valuable scientific advances have been made either by extending ordinary investigations to extreme lengths or by exploiting the borderlands between two so-called distinct sciences.

Geochemistry may be regarded as a combination of both these, for it extends the study of chemistry in space and time and temperature and it takes evidence from astronomy, biology and geology. It is of particular interest that it has been by the microchemical determination of the rarer components of ordinary rocks that GOLDSCHMIDT was able to rationalise the cycles of elements in space and time. Nearly all his work was done by quantitative emission spectroscopy and while it was rigorously controlled by comparison with synthetic specimens, it was of necessity limited in scope and by shortage of collaborators. A much more comprehensive survey of the possibilities of GOLDSCHMIDT's methods is being envisaged in the U.S. As a preliminary, a large amount of carefully mixed natural rock standards are being accumulated. These will ultimately serve as a more dependable control for spectroscopic methods, but from the interim report (*A Co-operative Investigation of Precision and Accuracy in Chemical, Spectrochemical and Modal Analyses of Silicate Rocks*, U.S. Geological Survey Bulletin No. 980, 1951) it is evident that much work on classical lines remains to be done before an adequate consensus of analytical opinion can be reached.

Microanalysis of Silicate Rocks. Part IV. The Determination of Alumina, by CHRISTINA C. MILLER, Ph.D., D.Sc., F.R.S.E., F.H.-W.C., and ROBERT A. CHALMERS, B.Sc.

The complications attending the classical method of determination of alumina in silicate rocks, and difficulties peculiar to the micro-scale, were reviewed. Earlier attempts by microchemists to devise an improved method for the determination of alumina were briefly described.

A new procedure was presented for the separation and direct determination of alumina in 5-mg samples of silicate rocks. Silica is eliminated by means of hydrofluoric and sulphuric acids, and the residue is fused with potassium bisulphate and extracted with acid. Several metals together are eliminated with cupferron and an organic solvent, and then aluminium is extracted as the acetylacetone complex, and finally converted into aluminium 8-hydroxyquinolinate.

Microchemical Determination of Sulphur in Organic Compounds, by WILLIAM H. MASSIE, B.Sc., Ph.D., A.R.I.C.

Organic compounds that contain nitrogen in addition to sulphur give, on combustion in oxygen over platinum, a non-quantitative yield of nitrous and nitric acids whose presence render worthless the simple and rapid micro-titrimetric procedure for sulphur as sulphuric acid.

A number of modified volumetric methods for the estimation of sulphur in this type of compound have been described, but none is completely satisfactory owing to involved technique or to defects inherent in the method.

A promising physico-chemical titrimetric method, supported by analytical results, was advanced as a suggestion for the direction of future work on this subject.

The Meeting was preceded by an afternooon visit to the Clydebridge Steel Works of Colvilles Ltd.

Ordinary Meeting of the Physical Methods Group

The Fortieth Ordinary Meeting of the Physical Methods Group of the Society of Public Analysts and Other Analytical Chemists was held at 6.30 p.m. on Tuesday, April 14th, 1953, in the Meeting Room of the Chemical Society, Burlingtion House, London W.1. This meeting was organised by the Polarographic Discussion Panel. Dr. J. HASLAM, Chairman of the Group, opened the meeting and invited Mr. G. W. C. MILNER, Honorary Secretary of the Polarographic Discussion Panel, to occupy the Chair for the rest of the meeting. About 42 members and visitors were present.

The following papers on *Polarography* were presented:—

The Polarographic Determination of Fluoride, by B. J. MACNULTY, Ph.D., B.Sc., F.R.I.C., G. F. REYNOLDS and E. A. TERRY.

Since it had already been shown that the effect of fluoride on the determination of aluminium was a sound basis for determination of the former publication by WILLARD and DEAN of the polarographic method for determining aluminium using pontochrome violet R.S. provised the basis for the polarographic determination of fluoride.

The method consists of measuring the effect of an unknown amount of fluoride on the polarographic step produced from a standard amount of aluminium and dye, and comparing the observed effect with that produced by known quantities of fluoride.

It has been shown using standard instruments that the effect of fluoride on the aluminium pontochrome violet polarographic step is quantitative down to 0.1 microgram/ml whilst the use of the cathode ray polarograph enables a lower limit for determination of fluoride in water solution of 0.001 microgram/ml to be reached.

In the latter case we have found it necessary to allow the solutions to stand for twenty-four hours prior to polarographing in order that the slowly attained equilibria in the solution may be reached, otherwise results are meaningless.

The method has been applied to the determination of fluoride in hydrochloric and hydrobromic acids, and bromine. Impurities which would otherwise interfere with the method (*e.g.* Al, Fe, etc.) are removed by shaking out with acetonyl acetone. In certain cases the minute amounts of impurities still present after shaking out prevent a flat top to the polarographic step being formed; this can be overcome by the addition of a small amount of cadmium.

When using the cathode ray instrument at full sensitivity considerable trouble was experienced due to vibration of the mercury pool, but the use of an external electrode avoids this.

The Amperometric Titration of Zinc and its Application to the Determination of Zinc in Lubricating Oils, by D. PICKLES, B.Sc., A.R.I.C., and C. C. WASHBROOK, A.R.I.C.

A method was described for the determination of zinc by amperometric titration with di-sodium ethylenediaminetetra-acetate (versene) in a strongly alkaline solution containing cyclohexylamine, or in a buffered solution containing ammonium acetate. The method is applied to the determination of zinc in new and used lubricating oils; interfering elements are either removed (copper, iron, barium, lead) or suppressed (calcium).

A Tentative Method for the Determination of Calcium by means of the Polarograph, by Mrs. BERTHA LAMB, B.Sc.

The direct determination of calcium polarographically presents a certain amount of difficulty because the choice of a base solution is restricted to the quaternary ammonium derivatives (owing to the high negative decomposition potential required — greater than minus 2.0 volts). The impurities frequently found in the base solution, *i.e.*, mono- di- and tri-methylamines, all have decomposition potentials in the same region as the calcium and therefore interfere with the determination of the calcium step.

In addition there appears to be some evolution of hydrogen which creates a change in the pH of the solution in the immediate vicinity of the dropping electrode, even in solutions where the initial pH was greater than 7. This causes inconsistencies and non-reproducible polarograms. The addition of lithium or barium hydroxide improves the shape of the waves and it is possible to determine calcium in concentrations ranging from 0.1 millimolar to 1.0 millimolar.

The final base solution consisted of 0.016 molar tetramethylammonium bromide (specially purified) and 0.0016 — 0.0032 molar lithium hydroxide. The concentration of lithium hydroxide has to be increased with increasing concentration of calcium to eliminate the maxima and other irregularities which occur. Further work using specially purified quaternary salts is continuing.

Ordinary Meeting of the Scottish Section

An ordinary Meeting of the Scottish Section of the Society of Public Analysts and Other Analytical Chemists was held at 7.15 p.m. on Friday, April 10th, 1953, in the George Hotel, George Street, Edinburgh 2, when a lecture on *Modern Methods of Analysis in the Training of the Student*
was presented by
Miss Christina C. MILLER, Ph.D., D.Sc., F.R.S.E., F.H.W.C.

The lecture was followed by an open discussion.

Synopsis of Lecture

The broad background against which the student must be taught was described, and the question of what the student should be taught, discussed. The training at Edinburgh University of the potential honours graduate was then outlined, with particular reference to the inorganic side, the lecturer's own domain.

Simple apparatus used by students for semimicro qualitative analysis, and for a few micro quantitative experiments, were shown. The lecture was illustrated by slides.

REVUE DES LIVRES

Inorganic Thermogravimetric Analysis, by CLÉMENT DUVAL. Elsevier Publishing Company, Amsterdam 1953, 531 pages, 152 figures, Prix: £ 3.

L'analyse thermogravimétrique n'avait, jusqu'à maintenant, jamais fait l'objet d'un ouvrage complet et détaillé. Cette lacune est désormais comblée et par une excellente traduction, rendue accessible au public de langue anglaise.

Dans une première partie, et après un bref historique de la méthode, celle-ci nous est présentée sous son aspect moderne d'une manière très approfondie. Le lecteur y trouvera la description de chaque partie de la balance thermique enregistreuse donnant d'une manière continue le poids d'un précipité en fonction de l'augmentation de température. Puis un important chapitre traite de l'emploi de l'instrument, de la précision des mesures et de l'interprétation des courbes obtenues. Les dernières méthodes gravimétriques et de nouveaux procédés de séparations sont exposés. Cette partie de l'ouvrage contient encore un chapitre traitant de l'analyse automatique qui permet de confier les dosages à des personnes non spécialisées. Quelques exemples d'étude de précipités binaires sont donnés.

La seconde partie est le résultat de l'étude de près de mille précipités dont les courbes sont discutées et interprétées d'une manière remarquable. Il y est consacré un chapitre pour chacun des 62 éléments et ions traités dans l'ouvrage. Dans chaque cas on trouvera les courbes obtenues par les réactifs inorganiques et organiques donnant les meilleurs résultats.

Ce livre s'adresse aussi bien aux minéralogistes qu'aux chimistes, il intéressera tous ceux dont les travaux comprennent ou dépendent d'analyses inorganiques et nous ne pouvons que le leur recommander.

J. VOGEL (Genève)

Ion Exchangers in Analytical Chemistry, by OLOF SAMUELSON. Almqvist & Wicksell, Stockholm, John Wiley & Sons Inc. New York, 1952, 291 pages, 47 figures.

Cet ouvrage, qui se divise en trois parties, traite d'une façon magistrale des échangeurs d'ions et de leurs applications en chimie analytique, tant minérale qu'organique et biologique.

Dans la première partie, l'auteur, spécialiste du sujet depuis de nombreuses années, expose les propriétés fondamentales des échangeurs d'ions (structures, équilibres, cinétique).

La deuxième partie traite des techniques de séparations par échangeurs d'ions dans l'analyse et en chromatographie.

Enfin, la troisième partie, la plus importante, est réservée aux applications pratiques des échangeurs d'ions dans les trois domaines principaux de l'analyse: minéral, organique et biochimique.

Ce livre, d'impression très soignée et de lecture facile, est agrémenté de nombreuses figures et graphiques et donne en outre une bibliographie complète jusqu'à fin 1951.

De part l'importance du sujet traité et ses nombreuses applications aux divers domaines de la chimie analytique, cet ouvrage sera certainement très apprécié de tous les chimistes ayant à résoudre les problèmes sans cesse plus complexes de l'analyse.

G. PERRET (Genève)

ANALYTICA CHIMICA ACTA

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SUBJECT INDEX

Chr. = Chromatography — chromatographie — chromatographische Analyse
Col. = Nephelometric and colorimetric analysis — Néphélométrie et colorimétrie — nephelometrische und kolorimetrische Analyse
Grav. = Gravimetric analysis — gravimétrie — gravimetrische Analyse
Id. = Identification reactions — identification (réactions) — Identifizierungsreaktionen
M. = Miscellaneous — divers — Verschiedenes
Pol. = Polarography — polarographie — Polarographie
Pot. = Potentiometric, conductometric, amperometric and coulometric analysis — potentiométrie, conductométrie, ampérométrie et coulométrie — potentiometrische, konduktometrische, amperometrische und coulometrische Analyse
Sp. = Spectrographic (spectrochemical) analysis — spectrographie — spektrographische (spektrochemische) Analyse
Vol. = Volumetric analysis — volumétrie — volumetrische Analyse

	Chr.	Col.	Grav.	Id.	M.	Pol.	Pot.	Sp.	Vol.
Adsorption					261				
Ag	344								
Al		384	378						
Ameisensäure									429
Amine sulfates					122				
sulphate(s)									
Aminés, acides				88					
Amino acids									
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